Studies on the Heat of Solution. I. Heats of Solution of Crystalline Pentaerythritol and Mesoerythritol

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Introduction

The measurement of heat of solution of crystalline materials is one of the useful methods for the determination of heat of formation of solid solution as well as of molecular compound, energy content of meta-stable modifications, energy of lattice imperfections, etc. Since we have hitherto investigated the interaction energies of different kinds of molecules constituting crystalline molecular compounds by the method of vapor pressure measurement[1] and also the interaction of water and other materials by differential thermal analysis and other methods[2], we have undertaken to study the heat of solution of crystalline materials in these connections.

As is well known, among the substances interacting with water, a group of alcohols exhibits strong hydrogen bond with water. Although the measurements of the heat of solution as well as the heat of dilution of the univalent alcohols, and some saccharides have been made, accurate determinations for polyvalent alcohols are very scanty. Now that the crystal structure as well as the thermal properties of pentaerythritol[3][4] and mesoerythritol[5] have been studied in considerable detail in our laboratory, we measured the heats of solution of these materials as the first step to the investigation on the heat of solution of crystals.

Experimental

(i) Apparatus and procedure: The calorimeter used is illustrated in Fig. 1. The calorimeter vessel consists of a silvered Dewar vessel (A) with a capacity of ca. 700 cc., containing the calorimeter heater (B), the glass stirrer (C), the dissolving device (D) for specimen under investigation and the junction points (E) of copper-constantan multiple thermocouple measuring the temperature variation of the calorimeter with reference to the average temperature of the inner water jacket (X). The Dewar vessel was mounted in a water-tight submarine jacket (F) which is made of 1 mm. thick copper sheet plated with chromium and polished on the surface. The air gap between the calorimeter vessel and the wall

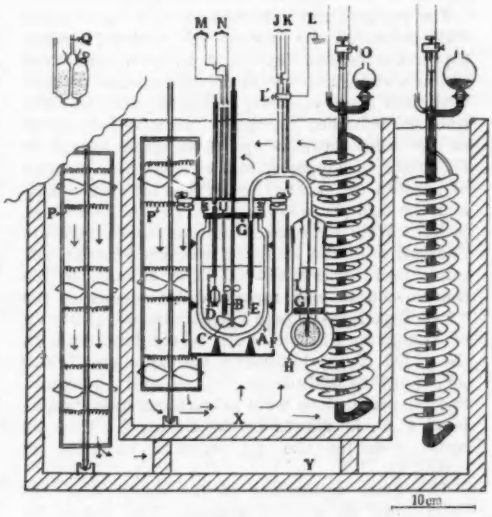

Fig. 1.

G: cork plate
I: lead block to avoid thermal leakage
J: main thermel measuring the temperature difference between calorimeter and fluctuation damper
K: thermocouple measuring the temperature difference between fluctuation damper and inner water jacket
L: earth to avoid leakage current
M: to voltmeter
N: to ammeter and battery
P: nichrome heater and stirrer

(1) I. Nitta, S. Seki, H. Chihara and K. Suzuki, *Sci. Paper Osaka Univ.*, No. 29 (1951); I. Nitta, S. Seki and H. Chihara, *J. Chem. Soc. Japan*, **70**, 387 (1949).

(2) I. Nitta and S. Seki, *J. Chem. Soc. Japan* **69**, 87 (1948); H. Chihara and S. Seki, This Bulletin, **26**, 88.

(3) I. Nitta and T. Watanabé, *Nature*, **140**, 365 (1937); I. Nitta and T. Watanabé, *Sci. Paper Inst. Phys. Chem. Research*, **34**, 1059 (1938); See also F. J. Llewellyn, F. G. Cox and T. H. Goodwin, *J. Chem. Soc.*, 883 (1937).

(4) a) I. Nitta, S. Seki and K. Suzuki, This Bulletin, **24**, 63 (1951); b) I. Nitta, S. Seki and M. Momotani, *Proc. Japan Acad.*, **26**, No. 9, 26 (1950); c) I. Nitta, S. Seki, M. Momotani, K. Suzuki and S. Nakagawa, ibid, No. 10, 11 (1950); d) I. Nitta, T. Watanabe, S. Seki and M. Momotani, ibid. No. 10, 19 (1950).

(5) I. Nitta, T. Watanabé and Y. Tomomatsu (unpublished).

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of the submarine jacket was about 1.5 cm. The heat conductivity constant between the calorimeter and the outer part was found to be 0.8 cal./min. deg.

The temperature fluctuation of the outer water jacket (Y) (ca. 40 litres) was controlled within the accuracy of ±0.002°C., while the inner water jacket within ±0.0003°C. A sensitive toluene-mercury regulator (O), efficient stirring device (P) (the circulation of whole water is accomplished in the period of 5~8 sec.), and a special electrical circuit for protection of oxidation of the mercury surface of the regulator were employed.

The temperature variation of the calorimeter was measured by means of twelve-junctions copper-constantan thermocouple, each junction of which was insulated with polystyrene and covered with thin glass capillary tubes separately. The standard reference junction points were introduced in the Swietoslawsky-type fluctuation damper[6] (H) made of copper sphere covered with a layer of paraffin (ca. 4 mm.) and a thin alminium foil, and the damper was immersed in the inner water jacket. With these constructions the temperature fluctuation of the standard reference junction was minimized to ±0.0001°C. The e. m. f. of the thermo-couple was measured by means of the "P-7 Type Low-voltage Potentiometer" (0.01μV.) of Yokogawa Electric Work in combination with the "RC Type Reflection Galvanometer" (0.2 μV./mm.) of Shimadzu Co. as null indicator. Special precautions were taken to exclude "vagabond e. m. f." caused in the circuit[7]. Thus we could measure the temperature variation of 0.0001°C.

The water equivalent of the calorimeter was determined by electric energy. The heater for this purpose is made of constantan wire (ca. 10 ohm) wound on thin mica strips and insulated with a thin layer of polystyrene. The ampere and the voltage drop were measured by precision type ammeter and voltmeter. The source of constant current is a heavy duty lead storage battery (120 A. H.), which is controlled to a steady state by discharge into the ballast resistor of approximately the same resistance as the heater for a period of an hour or more before use.

The stirrer was operated with steady speed D. C. motor. The stirring velocity was regulated at about 170 r. p. m. and the heat produced by stirring at this velocity was about 0.23 cal./min. The dissolving device made of hard glass has a capacity 5~10 cc. To dissolve the powdered specimen, the glass rod (Q) is pushed downward. The endothermic heat effect due to this operation, which may be ascribed to evaporation of water into the air bubbles escaping from the glass bulb, is found to be only about 0.3 cal. even for the largest vessel.

In every run, before the measurements, the calorimeter was immersed in the thermostat for about 3~5 hours after the temperature of thermostat reached the stationary value. For the determination of the heat quantity from the temperature-time curve, the correction of heat exchange between the calorimeter and the water jacket was made by use of Newton's heat flow equation, and the other corrections mentioned above were also taken into consideration.

In order to test the usefulness of the calorimeter, the heat of solution of NaCl was determined (see Table 1). The result obtained coincides within the accuracy of 0.7% with the most reliable values at the same conditions recommended by Bichowsky and Rossini.[8]

Table 1

t°C.	Substance	N	ΔH_{soln} (this research) kcal./mol.	ΔH_{soln} (others) kcal./mol.
18	NaCl	400	1.218	1.225±0.005
18	Pentaerythritol	4300	4.77	
		2200	4.78	
		1100	4.79	6.3[9]
		620	4.83	
18	Mesoerythritol	4600	5.24	5.54[10]

(ii) Materials;

(a) NaCl: The product of "for analysis" of Takeda Co. was desiccated by heating for about five hours under high vacuum (10^{-4} mm. Hg or less) at about 150°C.

(b) Pentaerythritol: The product of Shionogi Co. was recrystallized from aqueous solution four times and then subjected twice to fractional sublimation at about 180°C. under high vacuum (m. p. 264°C.).

(c) Mesoerythritol: The product of Kahlbaum Co. was purified by fractional sublimation under high vacuum at about 110°C. (m. p. 120.3°C.). The crystal exists in two modifications, stable and metastable, at room temperature. The present specimen is of stable form.

(iii) Experimental Results: The results obtained are all given in Table 1 together with some other reference data. In this table N in the third column is the mole number of water to dissolve one mole of solute and the sign of enthalpy is taken positive for endothermic process. Comparing our values with the data in the fifth column, obtained at higher concentrations by other investigators, it is evident that the heats of dilution for both substances are a little exothermic. It is also observed that the heat of solution of pentaerythritol becomes almost constant when the degree of dilution exceeds N=1000.

(6) W. Swietoslawsky, "Microcalorimetry", Reinhold Publishing Co., 1946.

(7) "Temperature, its Measurement and Control in Science and Industry", Reinhold Publishing Co., 1944, p. 265.

(8) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances", Reinhold Publishing Co., 1936.

(9) From temperature dependence of solubility (22~58°C, N=47~22) Cooke, *Paint. Manif.*, **18**, 125 (1948).

(10) M. Berthelot, *Ann. Chim. et Phys.* **26**, 201 (1892) (24°C, N=300).

Table 2

Substances	$-\Delta H^{\infty}_{soln}$ (or ΔH^{∞}_{mix})	ΔH_{subl} (or ΔH_{vap})	$-\Delta H^{\infty}_{hyd}$ (obs)	$-\Delta H^{\infty}_{hyd}$ calc. from (2) & (3)	$-\Delta H^{\infty}_{hyd}$ calc. from (5) & (6)
Ethylene Glycol	(1.7)	(14.9)	16.6	20.9	18.5
Glycerol	(1.5)	(20.0)	21.5	30.6	25.9
Mesoerythritol	−5.2	32.3 (22.3)	27.1	41.4	34.5
Pentaerythritol	−4.8	31.4 (19.2)	26.6	40.3	33.6

Discussion of Results

As mentioned above, the heats of dilution of both substances are exothermic. Recently, Lange and his coworkers[11] measured the heats of dilution of univalent alcohols, and saccharides, and found that they are exothermic similarly to what we found in the present experiment. They explained this exothermic effect to be ascribed to the dissociation of the associated solute molecules. Even though we have not obtained the data of heats of dilution accurately enough to permit us to draw a definite conclusion on the mechanisms of the dissociation of hydrogen bond of polyalcohols investigated, it seems very plausible to assume that the exothermic heats of dilution of the present materials would also be due to the dissociation of the dimer or higher associates.

Now, we should like to discuss further the hydration state of the polyalcohols. As is well known, the heat of hydration is given by the following relation:

$$\Delta H^{\infty}_{hyd} = \Delta H^{\infty}_{soln} - \Delta H_{subl}, \qquad (1)$$

where ΔH^{∞}_{hyd} indicates the heat of hydration at infinite dilution, ΔH_{subl} the heat of sublimation and ΔH^{∞}_{soln} the heat of solution of crystal to form infinitely dilute aqueous solution. If the substance to be dissolved is liquid, the heat of vaporization and heat of mixing take the places of heats of sublimation and of solution, respectively. In Table 2 we give ΔH^{∞}_{soln} (or ΔH^{∞}_{mix}), ΔH_{subl} (or ΔH_{vap}) and $-\Delta H^{\infty}_{hyd}$ of the substances investigated and of other related ones. The heats of solution listed in Table 1 may be regarded approximately as ΔH^{∞}_{soln} on account of the independence on the concentration as shown in the column 4. As to the heats of sublimation we have already reported.[5a)(5c)] The heats of mixing at infinite dilution of ethylene glycol[12] and glycerol[13] are estimated from the extrapolation of the data at higher concentrations to the infinite dilution. For the heat of vaporization of ethylene glycol, the data by Louguinine[14] at 90°C was adopted. For glycerol there is reported the temperature variation of vapor pressures by Stedman.[15] The calculated heat of vaporization from them (21.17 kcal./mole at 75°C), however, seems to be not so trustworthy on accont of the unreasonably large value in comparison with that of pentaerythritol (19.2 kcal./mole) and of mesoerythritol (22.3 kcal./mole), having four hydroxyl groups, and of abnormally high dependence of the heat of vaporization on the temperature. So, we estimated 20 kcal./mole for the heat of vaporization of glycerol (See Table 2).

According to Butler,[16] the heats of hydration of univalent alcohols may be calculated by the following semi-empirical equations (2) and (3),

$$\Delta H^{\infty}_{hyd} = \left\{ \frac{n}{2}\gamma_{W\text{-}W} - n_{W\text{-}CH}\gamma_{W\text{-}CH} - n_{W\text{-}OH}\gamma_{W\text{-}OH} \right\}, \qquad (2)$$

$$n = n_{W\text{-}CH} + n_{W\text{-}OH}, \qquad (3)$$

where n is the total number of water molecules hydrated to the solute molecule in question, $n_{W\text{-}CH}$ and $n_{W\text{-}OH}$ the number of hydrated water molecules for CH and OH groups respectively; $\gamma_{W\text{-}W}$ is the energy required to separate a single pair of water molecules, and $\gamma_{W\text{-}CH}$, $\gamma_{W\text{-}OH}$ the energies of interaction between a hydrated water and a CH or OH group, respectively. Putting somewhat artificial assumptions of

$$\gamma_{W\text{-}W}=5.25,\ \gamma_{W\text{-}CH_3}=3.4,\ \gamma_{W\text{-}CH_2}=3.4,$$
$$\gamma_{W\text{-}CH}=3.4 \text{ and } \gamma_{W\text{-}OH}=5.6, \qquad (4)$$

for the interaction energies (in kcal./mole), and $n_{CH_3}=3$, $n_{CH_2}=2$, $n_{CH}=1$ and $n_{OH}=3$ for the number of hydrated water molecules, Butler found that the calculated ΔH^{∞}_{hyd} values from the above equations are in good agreement with the observed values for normal univalent alcohols, and also that they are always larger by 0.8 kcal. per one branching than the observed data for branched alcohols. We have tentatively calculated the heats of hydration of polyvalent alcohols with application of these values and found indeed large positive deviations as shown in the fifth column in Table 2.

(11) E. Lange and H. G. Marlegraf, *Z. Electrochem.*, **54**, 73 (1950).

(12) a) International Critical Table. (average value of following two: Berthelot, (1882); de Forcrande, (1890).); b) F. Schwers, *Z. phys. Chem.*, **75**, 256 (1911).

(13) a) I. C. T. average value of Berthelot (1873, 1976), de Forcrande (1887, 1888), Gerlach (1884) and Kolossowsky (1913); b) Katz. *Proc. Amsterd. Acad.*, **13** 970 (1911) R. Fricke and J. Lücke, *Z. Electrochem.*, **35**, 636 (1929).

(14) W. Louguinine, *Ann. chim. et phys.* **26** 239 (1902); W. Hieber and A. Waerner, *Z. Electrochem.*, **40**, 252 (1934).

(15) D. F. Stedman, *Trans. Faraday Soc.*, **24**, 296 (1929).

(16) J. A. V. Butler, *Trans. Faraday Soc.*, **32**, 229 (1936).

Table 3

Substances	Molecular Volume	n	n'	θ'	θ'/θ_0	$q=\theta'/\theta$
Ethylene Glycol	55.6[a]	10	8.18	9.8	1.67	0.83
Glycerol	72.8[a]	14	10.08	13.1	2.28	0.73
Mesoerythritol	92.0[b]	18	12.22	16.9	2.90	0.71
Pentaerythritol	110.0[c]	20	14.22	16.2	2.77	0.69

a: Taken from reference[18].

b: We estimated the density of liquid from that of solid, assuming volume change on fusion is 10%.

c: As the present material belongs to the so-called plastic crystal (see reference[31]), we estimated the density of liquid from those of the two modification of solid, and heats of fusion and transition[4], using following relation:

$$\frac{\Delta V\,(\text{fusion})}{\Delta V\,(\text{transition})}=\frac{\Delta H(\text{fusion})}{\Delta H(\text{transition})}$$

To elucidate the nature of this deviation we have attempted to calculate $\Delta H^{\infty}_{\text{hyd}}$ of the polyvalent alcohols employing the experimental values of $\Delta H^{\infty}_{\text{hyd}}$ of a series of univalent alcohols and an other equation of some different meanings from that of Butler, instead of adopting somewhat artificial choice of n and γ values given above.

Supposing that the hydrated water molecules are not permanently fixed to the solute molecules owing to the thermal agitation, then the number n may be considered to have only a statistical meaning.[17] Accordingly this number may not necessarily be an integer as Butler has assumed. To create a cavity to hold a solute molecule in the liquid, the number of hydrogen bonds to be broken (n') will be 4, 6, 8, 10 and 12, if the volume of a cavity is 1, 2, 3, 4 and 5 integral multiples of that of a water molecule. It is possible, then, to determine the number n' from the ratio of the molecular volume of solute to that of water, using interpolation of above-mentioned relations between n' and molecular volume ratio. The numbers n' obtained in this way are given in Tables 3 and 4. (n' differs from n, and the relations to the heats of hydration of univalent alcohols are given in Fig. 2.) Then, inserting equation (3) into (2) and taking into account the effect of branching, we have

$$\begin{aligned}\Delta H^{\infty}_{\text{hyd}} &= n'\left\{\frac{1}{2}\gamma_{\text{W-W}}-\gamma_{\text{CH-W}}\right\}\\ &\quad -n_{\text{W-OH}}\{\gamma_{\text{W-OH}}-\gamma_{\text{W-CH}}\}\\ &\quad +\{\text{effect of branching}\}\\ &= n'\varphi-\theta+\delta \qquad (5)\end{aligned}$$

In this equation integral number n in (2) is replaced by n', and θ is proportional to the number of OH groups in the solute molecule if the intramolecular interaction between OH groups is negligibly small.

Table 4

Substances		n[16]	n'[18]	$-\Delta H^{\infty}_{\text{hyd}}$ (obs.)
Methyl	Alcohol	6	6.50	11.24
Ethyl	〃	8	8.46	12.88
Propyl-	〃	10	10.28	14.42
Butyl-	〃	12	12.14	15.94
Amyl-	〃	14	14.06	17.50
Iso propyl-	〃	10	10.46	13.45
Iso butyl-	〃	12	12.24	15.24
sec-Butyl-	〃	12	12.18	15.06
tert-Butyl-	〃	12	12.42	14.44
tert-Amyl-	〃	14	14.06	15.69

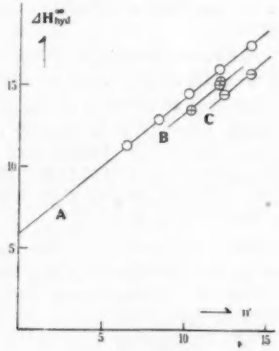

Fig. 2.

A: normal alcohols
B: one branched alcohols
C: two branched alcohols

As shown in Fig. 2 experimental data of normal, one-branched, two-branched univalent alcohols lie on three different straight lines. Thus, from these lines and equation (5), we obtain the following relations:

$$\varphi_0=-0.834,\ \theta_0=5.82 \text{ and } \delta_0=0.80/\text{branch}. \qquad (6)$$

(suffix $_0$ means the value of univalent alcohol)

(17) J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6** 666 (1941); J. A. Pople, *Proc. Roy. Soc.*, **A 205**, 163 (1951).

(18) J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds", Elsevier Publishing Co., 1950.

The reason for the appearance of the correction factor δ may be explained by the following; (i) as was pointed out by the present authors,[4a] the polarizabilities of the carbon atoms in branched hydrocarbons are somewhat smaller than that of the normal one, so the contributions of the dispersion and induction interaction energies become smaller; ii) in branched hydrocarbons the interatomic distances between hydrated water molecules and the inner carbon atoms are larger than that of the normal one, hence, the contribution to the interaction energy of these atoms becomes smaller.

Inserting n' values derived from the molecular volume of solute in liquid state into equation (5) under the assumption that the intramolecular interaction of OH groups is negligible and putting in the numerical values of equation (6), we obtain the heats of hydration of polyvalent alcohols given in the last column in Table 2. There remain still some deviations from the experimental values, although they are diminished considerably in comparison with the results obtained by the method of Butler. Certainly, the origin of these deviations is to be attributed to the intramolecular interaction of OH groups which gives rise to decrease of the number of hydration water molecules. The similar fact has been recently observed by Shimura.[19] He measured the electrostriction of water caused by dissolving various sorts of amino acids and found that, in comparison with the δ- or γ-amino acid the electrostriction caused by NH_3^+ group of α-amino acid is decreased. As a measure of decrement of intermolecular hydrogen bond forming powers of OH groups in the polyvalent alcohols, we have tentatively calculated the factor $q=\theta'/\theta$. Here θ' is given by use of equation (5) from the observed heat of hydration of polyvalent alcohol and the values of φ and δ of the univalent alcohols. The results are given in the last column of Table 3 which indicate evidently the intermolecular interactions decrease (intramolecular interaction increases) from ethylene glycol to pentaerythritol. As to the former, it has been found recently[20] that from the study of infra-red spectroscopy intramolecular hydrogen bond of this molecule in solution state is not so strong as expected before. On the other hand, the possibility of more frequent formation of the intramolecular hydrogen bond may be enhanced by the internal rotation about C-C single bond in the case of more complex polyvalent alcohols. This may, in part at least, explain the decreasing tendency of q-values given in Table 3.

(19) K. Shimura, *J. Agr. Chem. Soc. Japan*, **23** 31, 48 (1949); **24** 412 (1951).

Summary

(i) The heats of solution of pentaerythritol and mesoerythritol have been measured at 18°C and found to be both of endothermic. (4.77 kcal./mole and 5.24 kcal./mole).

(ii) The heats of dilution of both substances are of exothermic.

(iii) From the heats of sublimation and of solution, the heats of hydration were determined (26.6 kcal./mole for pentaerythritol and 27.1 kcal./mole for mesoerythritol).

(iv) It was found that the intramolecular hydrogen bonds cause considerable deviations from the improved Butler rule on the heats of hydration of alcohols.

In conclusion the authors wish to express their sincere thanks to Professor Nitta for his kind guidance throughout this work. The cost of this investigation was defrayed from the funds of Taniguchi Kôgyô Shôreikai as well as from the Scientific Research Expenditure Grant from the Ministry of Education to which the authors' thanks are due.

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20) R. Mecke, *Z. Electrochem.*, **52**, 269 (1948).
(21) S. Seki, *J. Chem. Phys.*, **18**, 397 (1950).

Spectrophotometric Determination of Camphor-aldehydes. I.

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Introduction

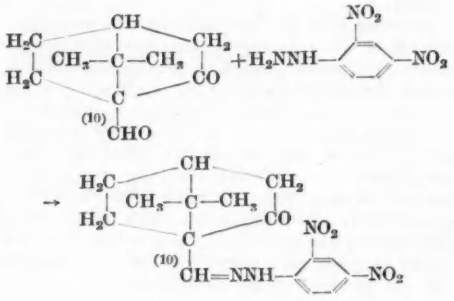
In 1934, the senior author and his co-workers[1] reported the results of their studies on the chemical synthesis of hydroxycamphors and their carbonyl derivatives. Afterwards, much progress in physiological and clinical aspects was made, thanks to the efforts of numerous investigators. In connection with the chemical and biological determination of their unstable camphor-aldehydes in O_2 atomosphere, many procedures have also been carried out by several authors, but twenty years have passed since that time, while no reliable reports have appeared about the physicochemical estimation of these camphor-aldehydes except those by ordinary iodometry, bisulfite-CrO_3 titration method etc. On the other hand, studies on electrophotometric assay of various compounds have been markedly improved, and it is especially well known that Roe[2],[3] and coworkers succeeded during 1942-4 in colorimetrically determining dehydro-ascorbic acid with 2,4-dinitrophenylhydrazine (DNP). Therefore, the authors have recently attempted to prepare pure 2,4-dinitrophenylhydrazones of β-oxocamphor and π-oxocamphor, in order to undertake spectrophotometric estimation of camphor-aldehydes with the standard crystals of their 2,4-dinitrophenylhydrazones. Experiments are outlined as follows:

1) The absorption spectra of β-oxocamphor-2,4-dinitrophenylhydrazone and π-oxocamphor-2,4-dinitrophenylhydrazone were exactly determined in isopropylalcohol solution by a Beckman spectrophotometer to give absorption maxima, $E^{1\%}_{1\,cm}$ 356 mμ=658 and $E^{1\%}_{1\,cm}$ 354 mμ=678, respectively.

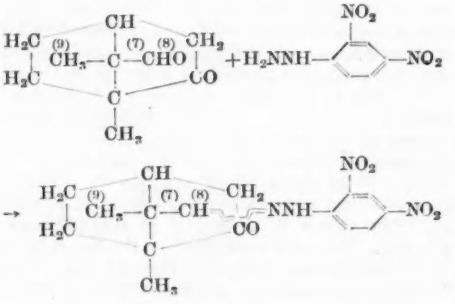
2) The E value of camphor-aldehyde-hydrazone in the solution to be tested was measured electrophotometrically, and the real amount of the camphor-aldehydes contained was calculated from the above standard E value.

(1) Y. Sahashi and co-workers, *Scient. Pap. Inst. Phys. Chem. Res.* **25**, 47 (1934).
(2) Roe, Kuether, *J. Biol. Chem.*, **147**, 399 (1943).
(3) A. Fujita, *Vitamins*, **4**, 53 (1951).

β(10) Apocamphor-1-aldehyde



π(8 or 9) Apocamphor-7-aldehyde



Experimental

(1) Preparation of Camphor-aldehyde-2,4-dinitrophenylhydrazones.—β (10) Apocamphor-1-aldehyde-2,4-dinitrophenylhydrazone: Freshly prepared crystals of β(10) apocamphor-1-aldehyde (β-oxocamphor) from β-(10) hydroxycamphor by means of chromic acid oxidation and sodium bisulfite purification were dissolved in alcohol and treated by hot saturated 5x HCl solution of 2,4-dinitrophenylhydrazine. After a few minutes heating, the hydrazone separated out as an insoluble amorphous precipitate which when recrystallized from hot alcohol formed yellow needle crystals, yield almost quantitative; m. p. 212°C. (uncorr.)

Found: C, 54.61, 54.67; H, 5.75, 4.90; N, 16.12, 16.34, Calcd. for $C_{16}H_{18}O_5N_4$: C, 55.46; H, 5.24; N, 16.18%

π(8 or 9) Apocamphor-7-aldehyde-2,4-dinitrophenylhydrazone: Crystals of π(8 or 9) apocamphor-7-aldehyde (π-oxocamphor), freshly prepared

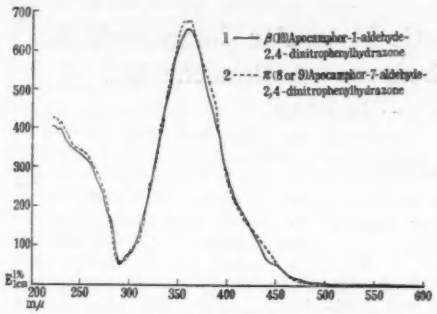


Fig. 1.—Absorption spectra of camphor-aldehyde-2, 4-dinitrophenylhydrazone in isopropylalcohol.

from π-bromocamphor according to Sahashi's method, were dissolved in alcohol and treated with hot saturated 5N HCl solution of 2, 4-dinitrophenylhydrazine by the same process mentioned above. The amorphous precipitate thus obtained was recrystallized from hot alcohol, yielding yellow needle crystals in a quantitative amount; m. p. 202°C. (uncorr.)

Found: C, 55.29, 55.49; H, 4.82, 5.09; N, 16.04, 16.01, Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.46; H, 5.24; N, 16.18%

(2) **Spectrography of Camphor-aldehyde-2, 4-dinitrophenylhydrazones.** — 100 γ of camphor-aldehyde-2, 4-dinitrophenylhydrazone to be tested were dissolved in 10 cc. of isopropyl alcohol. The standard absorption of the above compounds were measured by a Beckman spectrophotometer with the following results.

	β(10) Apocamphor-1-aldehyde-2, 4-dinitrophenyl-hydrazone	π(8 or 9) Apocamphor-7-aldehyde-2, 4-dinitro-phenylhydrazone
Absorption-maxima	$E^{1\%}_{1cm}$	$E^{1\%}_{1cm}$
	356 mμ=658	354 mμ=678

(3) **Analytical procedure.—DNP Reagent:** 5g. 2, 4-dinitrophenylhydrazine (DNP) were dissolved in 200 cc. hot 5N HCl solution and filtered after cooling.

Procedure: A) 1 cc. of aq. β(10) oxocamphor solution was refluxed for about a minute with 10 cc. of the DNP reagent and allowed to cool. After 30 minutes the yellow precipitate was filtered, washed with water and dissolved in 100 cc. isopropyl alcohol. The solution thus obtained was diluted up to 10 γ/cc. (2000 cc.) The extinction was then measured by a Beckman spectrophotometer.

B) 1 cc. of aq. π (8 or 9) oxocamphor solution was heated for about a minute with 10 cc. of DNP reagent and treated as mentioned above. The separating hydrazone was dissolved in 100 cc. of isopropyl alcohol and diluted up to 10 γ/cc. (1000 cc.) The Beckman photometric observation was then carried out in the ordinary way.

Calculation: β(10) oxocamphor: Found, $E^{1\%}_{1cm}$ 356 mμ=528

$$\text{Hence, } 10\gamma\times\frac{528}{658}\times 2000 = 16.04 \text{ mg.}$$

$$16.04\times\frac{166}{346} = 7.69 \text{ mg./cc.}$$

π(8 or 9) oxocamphor: Found, $E^{1\%}_{1cm}$ 354 mμ= 488

$$\text{Hence, } 10\gamma\times\frac{488}{678}\times 1000 = 7.19 \text{ mg.}$$

$$7.19\times\frac{166}{346} = 3.44 \text{ mg./cc.}$$

C) Cases where the solution to be tested contains other emulsifying organic agents such as Tween, Span etc., it is best to carry out the separation of camphor-aldehydes by the process of steam distillation, and DNP reagent must be added to the distillate.

Summary

1) 2, 4-dinitrophenylhydrazones of β(10) apocamphor-1-aldehyde and π(8 or 9) apocamphor-7-aldehyde were prepared and their absorption spectra were exactly determined.

2) From the standard E values, the amount of the above compounds in an unknown solution can be calculated from the estimation by a Beckman spectrophotometer.

The authors wish to express their sincere thanks to Dr. M. Yoshida for Beckman-photometry.

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Peculiarity of Dichroism of Aromatic Molecular Compounds. II. The Dichroisms of *s*-Trinitrobenzene—Anthracene and 4, 4′-Dinitrodiphenyl—Diphenyl

By Kazuo NAKAMOTO

(Received June 27, 1952)

Introduction

An earlier paper of this series[1] is concerned with dichroism of typical molecular compounds and the general rule regarding the dichroism of the first band principally due to the π-electrons of the benzene rings. That is, the absorption by the light with the electric vectors vibrating perpendicular to the molecular planes of both the components is always bathochromic and hyperchromic to the absorption by the light with those vibrating parallel to those planes. So, in the present investigation, measurements of dichroisms of molecular compounds, *s*-trinitrobenzene—anthracene and 4,4′-dinitrodiphenyl—diphenyl have been made in visible and ultraviolet regions, and their results have been discussed applying the general rule stated above.

Experimental

Materials.—(1) *s*-Trinitrobenzene—Anthracene—Fine orange acicular crystals are produced by mixing the methanol solutions of both the components in the molar ratio of 1:1, and allowing the solution to evaporate at room temperature. M. p. 164°. Monoclinic system. Straight extinction. This substance shows dichroism; orange, when viewed with linearly polarized light whose electric vector vibrates parallel to the *c*-axis (needle axis) and light yellow, when observed with those vibrating parallel to the *b*-axis.

(2) (4, 4′-Dinitrodiphenyl)$_2$—Diphenyl—Pale yellow acicular crystals are prepared by mixing the hot acetone solutions of both the components in the molar ratio of about 3:1 and allowing the solution to cool gradually. Monoclinic system. A striking characteristic of this crystal is that it has no clear melting point, owing to continuous decomposition with the elevation of temperature.[2] Straight extinction. Dichroism can not be observed with the naked eye.

Measurements.—Dichroisms of the crystals have been quantitatively measured by the microscopic method with microcrystals, as described in the former paper.[3]

Results and Discussion

(1) ***s*-Trinitrobenzene—Anthracene.**—In 1932, Briegleb and Schachowskoy[4] studied the absorption spectrum of this molecular compound in chloroform solution and calculated the heat of dissociation from their spectroscopic data. As to the crystal structure, Hertel and Römer[5] have inferred the orientation of both the molecules from the observed values of the lattice constants alone, and no further report has been presented.

Fig. 1 records the absorption spectra by linearly polarized lights with the electric vectors vibrating parallel to the *c*- and *b*-axes, respectively. The absorption curve of pure anthracene crystal by ordinary light is also shown for comparison (Curve 4). Absorption curves of both the components (Curve 1 and 2) and the molecular compound (Curve 3)[4] in liquid state are given in Fig. 1. From the comparison of the absorption curves in crystalline state with that of the components in solution, it is evident that the bands at 500~400 mμ in crystalline state consist mainly of the

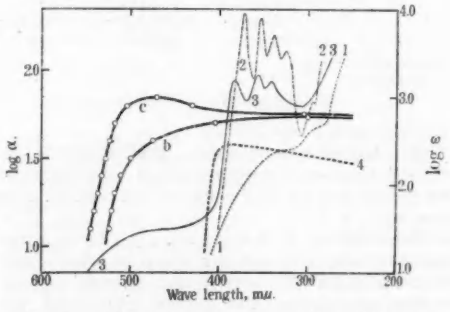

Fig. 1.—Absorption spectra of *s*-trinitrobenzene-anthracene and its components: 1, *s*-trinitrobenzene; 2, anthracene; 3, *s*-trinitrobenzene-anthracene; 4, anthracene in crystalline state (by ordinary light).

(1) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952).
(2) K. Suzuki, Presented before the Division of Structural Chemistry at the 4th Meeting of the Japan Chemical Society, Tokyo, April, 1951.
(3) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 390 (1952).
(4) G. Briegleb and T. Schachowskoy, *Z. physik. Chem.*, B **19**, 255 (1932).
(5) E. Hertel and G. H. Römer, ibid., B **11**, 77 (1931).

absorption due to the π-electron system of aromatic rings of both the molecules. It should be noted that these bands absorb the same region with the characteristic band of the molecular compound in Curve 3. As already discussed in the former work,[1] all of these absorptions at 500~400 mμ are essentially attributed to the intermolecular charge-transfer spectra resulting from an inter-benzoid overlap of the π-orbitals. Curve 3, however, does not indicate any distinct maximum since the anisotropic absorption in crystalline state is reduced by random orientation of molecules in liquid state.

As is shown in Fig. 1, the *c*-absorption is bathochromic and hyperchromic to the *b*-absorption. This result offers a further evidence to support the validity of the general rule for the dichroism of molecular compounds, if we accept the crystal structure predicted by Hertel and Römer for this compound. In other words, the *c*-absorption is bathochromic and hyperchromic to the *b*-absorption, because both the component molecules are piled up alternately along the *c*-axis making their molecular planes parallel to each other and the overlap of the π-orbitals that are thrust out perpendicularly from each molecular plane occur along the *c*-axis. We have, therefore, shown conclusively that the dichroism of this molecular compound can be interpreted by the general rule described before.

(2) **(4,4'-Dinitrodiphenyl)$_x$—Diphenyl.**—Since 1946, Saunder and his co-workers[6] have studied the crystal structure of molecular compounds of 4,4'-dinitrodiphenyl with various substituted diphenyls. According to their results, all of these compounds have a definite type of structure in which dinitrodiphenyl molecules form layers in face-centred array and lie one above another with a spacing of about 3.7 A. In a continuous arrangement of these layers, long tubular cavities are left running through the structure, and the other component molecules occupy these cavities and lie nearly normal to the planes containing dinitrodiphenyl molecules. The orientations of both the molecules in the crystal are shown graphically in Fig. 2. That is, these compounds have a peculiar structure which is quite different from that of typical molecular compounds. Moreover, based on the measurements of the closest intermolecular distance of approach, Saunder and his co-workers concluded that there is no localized bonding between the component molecules. So it is expected that the dichroism of such a compound will be considerably modified as compared with that of typical molecular compounds.

In the present paper, one of these molecular compounds, (4,4'-dinitrodiphenyl)$_x$—diphenyl, is selected and its dichroism has been measured in the ultraviolet region. Absorption spectra by linearly polarized lights with the electric vectors vibrating parallel to the *b*- and *c*-axes, respectively, are shown in Fig. 2, and their numerical data are given in the following table.

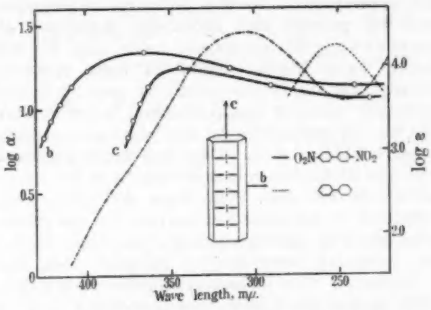

Fig. 2.—Absorption spectra of 4,4'dinitrodiphenyl-diphenyl: ——·——, 4,4'-dinitrodiphenyl; ----, diphenyl.

Table

	λmax. (mμ)	log αmax.
b-abs.	365	1.34
c-abs.	345	1.24

The spectra of both the components in alcoholic solutions are also marked in the same figure.

According to Niekerk and Saunder,[7] in the crystal of this compound, dinitrodiphenyl molecules are nearly parallel to the (001) plane, whereas diphenyl molecules are nearly normal to it and lie on the (010) plane. Comparing these results with our spectroscopic data, we may conclude that the *b*-absorption is the spectrum by the light whose electric vector vibrates parallel to the molecular plane of dinitrodiphenyl and perpendicularly to that of diphenyl. On the other hand, the *c*-absorption is the spectrum by the light whose electric vector vibrates perpendicularly to the molecular planes of dinitrodiphenyl and parallel to that of diphenyl.

So far, it is impossible to analyze these bands into the two absorptions due to dinitrodiphenyl and diphenyl, respectively. As is shown in the spectra of both the components in solution, however, dinitrodiphenyl (λmax, 308 mμ; log εmax, 4.39) is far more bathochromic to diphenyl (251 mμ; 4.26). It is reasonable to assume that this relation holds also for the spectra of both the components in crystalline state. Moreover, according to the stoichiometrical consideration of the mixing ratio in this compound, dinitrodiphenyl is expected to play a main rôle in the dichroism of the crystal. Thus, in the longer wave length region of these spectra, both the *b*- and *c*-absorptions can be assumed to consist principally of the absorption due to dinitrodiphenyl.

The fact that the *b*-absorption is bathochromic

(6) D. H. Saunder, *Proc. Roy. Soc. London*, **A 188**, 31 (1946).

(7) J. N. van Niekerk and D. H. Saunder, *Acta Cryst.*, **1**, 44 (1948).

and hyperchromic to the c-absorption suggests that the general rule about the dichroism of common aromatic crystals[8] holds also for the longer wave length region in these spectra. Namely, the absorption which is parallel to the molecular plane of dinitrodiphenyl is bathochromic and hyperchromic to the absorption which is perpendicular to it. Thus, the results obtained from the dichroism measurement have led us to the conclusion that there does not exist $\pi-\pi$ attraction in the direction normal to the molecular plane of dinitrodiphenyl. In other words, the foregoing consideration suggests that the dichroism of this molecular compound is explicable on the assumption that it is only a kind of mixed crystals except that it has a definite combining ratio determined solely by the geometrical consideration in crystal structure.

Summary

Measurements of the dichroisms of molecular compounds, s-trinitrobenzene—anthracene and 4,4′-dinitrodiphenyl—diphenyl have been made quantitatively made in the visible and ultraviolet region. It can be concluded that the crystal of the former compound has the same dichroic property as the typical molecular compound already given in the previous report. The dichroism of the latter compound suggests that there exists no special attraction in the direction normal to the molecular plane of dinitrodiphenyl.

The author wishes to express his sincere thanks to Prof. R. Tsuchida for his kind guidance and encouragement throughout this work. Appreciation is also expressed to Mr. K. Suzuki for the gifts of 4,4′-dinitrodiphenyl and diphenyl used in this research.

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(8) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 392 (1952).

Spectrochemical Study of Microscopic Crystals. III. The Dichroisms of μ-Peroxo-Dicobalt Compounds

By Shoichiro YAMADA, Yoichi SHIMURA and Ryutaro TSUCHIDA

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It has been known since long ago that compounds containing the atoms of the same element in different valency states often show extraordinarily deep colors. Although the phenomena have attracted the attention of many investigators, and speculative views were also proposed on the phenomena,[1],[2] no direct research, based upon the absorption spectra of those compounds in the crystalline state, has ever been reported.

This work was initiated to clarify the above phenomena with the aid of their absorption spectra and further to investigate the nature of the chemical linkages in these compounds. For this purpose decammine-μ-peroxo-dicobalt compounds were selected. These compounds, which have two metal atoms of the same element combined through a peroxy radical, present an adequate model for those more complicated compounds in which would exist the above supposed mutual interaction between two metal atoms through a negative ion.

In the present work the dichroisms of decammine-μ-peroxo-cobalt (III)-cobalt (IV) nitrate and of decammine-μ-peroxo-dicobalt (III) nitrate dihydrate have been measured, and the results obtained from the above measurements have been discussed.

Experimental

Materials. (1) **Decammine-μ-peroxo-cobalt (III)-cobalt (IV) nitrate,** $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5$.—This compound was prepared as dark green acicular crystals according to the direction of Werner and Mylius.[3] The crystals exhibit a

(1) See, for examples, E. H. Riesenfeld, "Lehrbuch der anorganischen Chemie," Rascher Verlag, Zürich, Switzerland, 1943, p. 573; H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," George Routledge and Sons, Ltd., London, England, 1940, p. 139.

(2) J. Whitney and N. Davidson, *J. Am. Chem. Soc.*, **69**, 2076 (1947); H. McConnell and N. Davidson, ibid., **72**, 3168 (1950), etc.

(3) A. Werner and A. Mylius, *Z. anorg. Chem.*, **16**, 245 (1898).

remarkable dichroism, i. e., they appear pale brownish yellow by polarized light with electric vector parallel to the direction of elongation and indigo blue by that perpendicular to the above. Acidic aqueous solutions of the compound, which appear dark blue, are comparatively stable, while neutral or alkaline solutions spontaneously decompose. The dichroism measurement of the crystal was made in the prism face.

(2) Decammine-μ-peroxo-dicobalt (III) nitrate dihydrate, $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_4\cdot 2H_2O$.—Dark greenish brown crystals were prepared by the method of Werner and Mylius.[3] These show a marked dichroism, i. e., brown by polarized light with electric vector parallel to the direction of elongation of the crystal, and bluish green by that perpendicular to the above. This compound is so unstable in aqueous solutions, acidic,[4] neutral or alkaline, that the absorption spectrum in solution could not be measured.

Measurements.—Quantitative dichroism measurements of the crystals were performed by the microscopic method[5] in the region covering 7500 to 2300 A. The //- or $\perp$-absorption in the figures denotes, respectively, absorption with electric vector perpendicular or parallel to the direction of elongation of the crystals.[6] α represents absorption coefficient per mm. of the crystal.

The absorption spectrum of the aqueous solution, slightly acidified with dil. sulfuric acid, was determined with a Beckman model DU quartz spectrophotometer in silica cells having a 1 cm. light path. Extinction coefficients were calculated from the equation

$$\varepsilon = 1/\mathrm{cd}.\log(I_0/I).$$

Measurements were made at room temperature. The complete spectrum was obtained from 8000 to 2200 A. Aqueous solutions of the complex salt were used at concentrations of 5.82×10^{-4} and 5.82×10^{-5} F.

Results and Discussion

Absorption Spectrum of the Aqueous Solution.—Results of the measurements with the aqueous solution are shown in Fig. 1 and Table 1. There have been published a few reports concerning absorption spectra of cobaltic polynuclear complexes in solutions. Shibata and Ohyagi reported the qualitative absorption curves of polynuclear

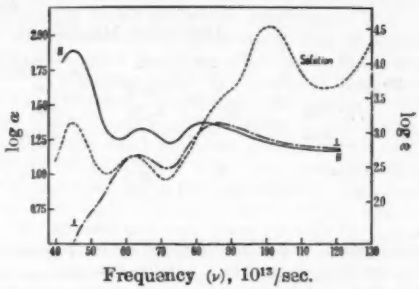

Fig. 1.—Dichroism of the crystal of $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5$ and absorption spectrum of the aqueous solution (dotted curve).

complexes in aqueous solution[7] and in phosphoric acid.[8] One of the present authors and Kuroya[9] reported absorption spectra of $[Co\{(OH)_2Co\ en_2\}_3](NO_3)_6$, $[Co\{(OH)_2Co(NH_3)_4\}_3]Cl_6$ and $[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4$, and found that polynuclear complexes of such a type generally display a "third band,"[10] caused by ligandolysis,[11] the dissociation of NH_3 in coordination into NH_2^- and H^+, at $\nu=100$ to 110×10^{13}/sec. and $\log\varepsilon=3$ to 4, besides two absorption bands corresponding to the first and the second absorption band.[10] Consequently, the absorption band at $\nu=101$ in the absorption spectrum of $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5$ is considered to be a "third band."

According to the previous report, monoaquo- and monohydroxy-pentammine cobaltic complexes show the first band at $\nu=$about 60 and hexammine cobaltic salt at $\nu=64-65$. Since binuclear complexes should show the corresponding absorption band at longer wave length than related uninuclear complexes,[12] it is supposed that the absorption band at $\nu=62.6$ is the second absorption band and the band at $\nu=44.6$ corresponds to the first absorption band. Besides those absorption bands as discussed above, there can be found an inflexion at $\nu=88$. This inflexion should be attributed to the peroxy group and may well be named the "peroxy-specific band," since the solutions of binuclear complexes with a peroxy radical as a bridge[8] exhibit a similar inflexion or a separated band at $\nu=$about 90 and $\log\varepsilon=$about 3.

It is seen that the ε_{max} of the first absorption band is considerably larger than that of the

(4) Decomposition of the compound was observed even in phosphoric acid solution.

(5) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Zoshindo Co., Osaka, Japan, 1944, p. 180. See also the previous reports of this series (R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 619 (1938); S. Yamada and R. Tsuchida, ibid., **25**, 127 (1952)).

(6) As will be shown in the later part of the present paper, the //-or $\perp$-absorption corresponds to the absorption with the electric vector vibrating parallel or perpendicular to the Co-O-O-Co direction.

(7) Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **37**, Art. 8, 19 (1916); *J. Chem. Soc. Japan*, **38**, 99 (1917).

(8) Y. Ohyagi, This Bulletin, **15**, 186 (1940).

(9) R. Tsuchida and H. Kuroya, ibid., **15**, 427 (1940).

(10) As to the first, the second and the third absorption band, see for example, R. Tsuchida, This Bulletin, **13**, 388 and 436 (1938).

(11) R. Tsuchida and M. Kobayashi, *J. Chem. Soc. Japan*, **64**, 1268 (1943); L. Tschugaev, *Z. anorg. Chem.*, **137**, 1401 (1924); G. Urbain, *Bull. soc. chim.*, **51**, 853 (1932); G. Okamoto, *J. Chem. Soc. Japan*, **57**, 1175 (1936); T. Uemura and H. Sueda, This Bulletin, **10**, 50 and 85 (1935), etc.

(12) See, for example, ref. (5), p. 159.

Table 1

Absorption Maxima of $[(NH_3)_5Co\text{-}O\text{-}O\text{-}Co(NH_3)_5](NO_3)_5$

	1st Band		2nd Band		O_2-Band		3rd Band	
Crystal	ν	$\log \alpha$	ν	$\log \alpha$	ν	$\log \alpha$		
//-abs.	45	1.88	64.6	1.32	82.6	1.38		
$\perp$-abs.			63.0	1.13	86.8	1.38		
Solution	ν	$\log \varepsilon$	ν	$\log \varepsilon$	ν	$\log \varepsilon$	ν	$\log \varepsilon$
	44.6	3.14	62.6	2.66	(88)	(3.5)	100.8	4.54

second band, which seems unusual as compared with previous data. This will be discussed in the later part of the present report along with the dichroisms of the crystals.

It is found that the compound is greatly bathochromic to the hexol and the diol complexes which contain bridging OH^- radicals. This shows that bathochromic effect of a peroxy radical is larger than that of OH^-.

The Dichroisms of the Crystals. (1) $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5$.—The dichroism of the crystal of the compound is shown in Fig. 1 and the data are tabulated in Table 1. The crystal exhibits the first, the second and the "peroxy-specific" absorption band, but lacks the third band, which is found in the absorption spectrum of the solution and observed to be considerably large as compared with the other bands. Comparing the absorption in the crystalline state with that of the aqueous solution, it is found that in the //-absorption the band at $\nu=45$ corresponds to the first band, the one at $\nu=64.6$ to the second band, and the one at $\nu=82.6$ to the peroxy-specific absorption band. Similarly, in the $\perp$-absorption the band at $\nu=63$ represents the second absorption band and the one at $\nu=86.8$ the peroxy-specific absorption band, the first band being so weak that it could be assumed that the band has no component in that direction.

The dichroic nature is found in any of the first, the second and the peroxy-specific band. Above all, exceedingly large dichroism is recognized in the first absorption band. Comparing the two characteristic directions, the Co-O-O-Co direction and that perpendicular to the above, a larger electric moment is expected in the former than in the latter. In consequence, the dichroism measurement shows that the direction, Co-O-O-Co, in the complex should be perpendicular to the direction of elongation of this crystal. The remarkable dichroism in the first band shows the far more frequent transition of d-electrons in the direction of the linkage, Co-O-O-Co, than in the direction perpendicular to the linkage. And the different features of the first and the second absorption band suggest the different origins of these bands.

(2) $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_4\cdot 2H_2O$. — The dichroism of the crystal is shown Fig. 2 and Table 2. Similarly as in the cobalt (III)-cobalt (IV) complex, the crystal shows the first, the second and the peroxy-specific band, but the third band, which should be exhibited by the aqueous solutions, was not observed. From a similar consideration as in the case of the cobalt (III)-cobalt (IV) complex, it is found that the band at $\nu=46$ in the //-absorption is the first absorption band. The broad and flat band at $\nu=60$ to 80 may be considered to be superposition of the second and the peroxy-specific band. Similarly, the band at $\nu=48$ in the $\perp$-absorption is the first absorption band, the one at $\nu=63$ the second absorption band, and the one at $\nu=83$ the peroxy-specific absorption band.

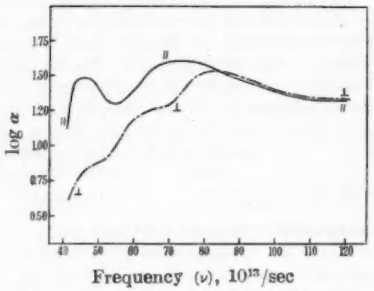

Fig. 2.—Dichroism of the crystal of $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_4\cdot 2H_2O$.

Table 2

Absorption Maxima of $[(NH_3)_5Co\text{-}O\text{-}O\text{-}Co(NH_3)_5](NO_3)_4\cdot 2H_2O$

	1st Band		2nd Band		O_2-Band	
	ν	$\log \alpha$	ν	$\log \alpha$	ν	$\log \alpha$
//-abs.	46.0	1.48	flat (superposed)			
$\perp$-abs.	(48)	0.85	(63)	(1.2)	83.0	1.53

The dichroism is observed in any of those bands. The dichroism as to the first band appears especially marked. Electric moment responsible for the first absorption band, which is supposed by the present authors to originate from transitions in an incomplete transition shell of the central cobaltic ions, would be larger in the Co-O-O-Co direction than in the direction perpendicular to the above. Therefore, it may be presumed that in the crystal the complex ions are arranged so that the Co-O-O-Co direction is almost perpendicular to the direction of elongation.

General Features of the Dichroisms.—Both the complexes in the crystalline state as well as in solution are bathochromic to the diol, the hexol

and related complexes which have two OH-radicals as bridges. This indicates that the peroxy radical usually exerts larger bathochromic effect than the hydroxy radical.

The crystals of both compounds lack the third band which should usually be observed in solution at ν=about 100 and log ε=3~4. This shows that the said band may be attributed to such a ligando-lysis, as is greatly favoured by interaction of solvent molecules with ligands of the complex ions. It is possible to suppose that ammonia molecules in the complex ion, which may be rather labilized under the influence of the peroxy radical in the complex, would be much more easily dissociated when the solvent molecules approach the ions, and that the band would disappear in the crystalline state where there exists no interaction of solvent molecules.

The two complex ions, μ-peroxo-dicobalt (III) and μ-peroxo-cobalt (III)-cobalt (IV) ions, have a similar configuration having two metal atoms connected through a peroxy radical. From the results of their dichroism measurements the following rules may be obtained for the dichroism of complexes of the above type:

(1) The first absorption band. The //-absorption, the absorption with the electric vector vibrating along the Co-O-O-Co direction, is remarkably hyperchromic to the $\perp$-absorption, the absorption with the electric vector vibrating perpendicularly to the above.

(2) The second absorption band. The //-absorption is hyperchromic and hypsochromic to the $\perp$-absorption.

(3) The peroxy-specific absorption band. The //-absorption is bathochromic to the $\perp$-absorption,[13] extinction coefficients of both absorptions being almost equal.

Interaction between Central Metallic Ions through a Bridging Peroxy Group.—Examining the absorption curves as presented in this report, it is found that the first absorption band of peroxy-cobalt (III)-cobalt (IV) nitrate is different from what the so-called first band should be, since (1) the first band in aqueous solution is about three times as strong as the second absorption band, which differs from the empirically derived tendency[14] that the first band of a cobalt (III) complex in solution is almost as strong as the second band, (2) in the //-absorption of the crystal, too, the first band is about three times as strong as the second band, which represents a quite unusual case with the absorption spectra of crystals, and (3) the first band of the //-absorption is extraordinarily hyperchromic to that of the $\perp$-absorption, the latter having a negligibly small extinction coefficient.

From the above discussions, and considering the fact that the absorption with the electric vector vibrating along the Co-O-O-Co direction should be much larger than the absorption with the electric vector perpendicular to the above, it may be supposed that two cobalt atoms of different valency states exert an interaction upon each other through a peroxy-radical between them; one may think that electrons vibrate back and forth between the two cores through a peroxy-radical as a bridge, and that in the ground state two cobalt atoms may not be distinguishable.

The previous data on absorption spectra of coordination compounds indicate that, generally speaking, complexes of a metal of a higher oxidation number show their absorption bands at shorter wave length regions than the corresponding ones of the same metal of a lower oxidation number. The absorption curves of the compounds reported in the present paper are inconsistent with the above tendency derived with most compounds. Thus comparing the μ-peroxo-cobalt (III)-cobalt (IV) complex with the μ-peroxo-dicobalt (III) complex, the former is not hypsochromic but even slightly bathochromic to the latter. This discrepancy also suggests the unusualness of the former compound and the possibility of the strong interaction between the central metallic ion as described above.

In the case of the μ-peroxo-dicobalt (III) complexes, too, the difference in α of the first band between the //- and the $\perp$-direction is so large that it may be possible to expect a sort of interaction between central metallic ions through a peroxy radical in the Co-O-O-Co direction. As is clear from the above descriptions, however, the interaction seems much large in the Co (III)-O-O-Co (IV) direction than in the Co (III)-O-O-Co (III) direction. This can also be understood from electronic configurations of cobalt ions. That is, since Co (III) has a $3d^6$ configuration and Co (IV) has a $3d^5$ configuration, it is probable that the said interaction in the μ-peroxo-Co (III)-Co (IV) complex is much stronger than in the Co (III)-Co (III) complex.

The same applies for similar Fe (II)-Fe (III)-polynuclear complexes, since Fe (II) and Fe (III) are isoelectronic, respectively, with Co (III) and Co (IV). Thus, in the magnetite, Fe_3O_4, and the prussian blue, K Fe Fe $(CN)_6$, mutual interactions between Fe (II) and Fe (III) are expected through an oxygen ion or a cyanide ion, which would cause anomalies in optical and magnetic properties of those compounds.

It is also suggested that a similar explanation holds for those compounds of a similar type which contain atoms of the same element in different valency states and exhibit unusual colours, and that the interaction of the above type between metallic ions through a bridging ion or radical represents a favourable and adequate model for processes in those more complicated compounds.

(13) This tendency resembles the rule observed about the dichroism of the π band of the benzene ring (cf. R. Tsuchida, M. Kobayashi and K. Nakamoto, *J. Chem. Soc. Japan*, **70**, 12 (1949); K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 390 (1952)), which may suggest that the electronic state of O-O- in those complexes is rather similar to that of the π-linkage in the benzene ring.

(14) H. Kuroya, *J. Inst. Polytech., Osaka City Univ.*, **1**, No. 1, Ser. C, 29 (1950); K. Sone, *J. Chem. Soc. Japan*, **71**, 270 (1950).

Summary

(1) The dichroisms of decammine-μ-peroxo-dicobalt (III) nitrate dihydrate, $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_4 \cdot 2H_2O$, and of decammine-$\mu$-peroxocobalt (III)-cobalt (IV) nitrate, $[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5](NO_3)_5$, and the absorption spectrum of the latter in aqueous solution have been quantitatively measured.

(2) The empirical rules on the dichroisms of those crystals have been obtained.

(3) The considerations on the absorption spectra of the above compounds have led to the conclusions that there exists a kind of mutual interaction between metallic ions through a bridging peroxy-radical and that the interaction between Co (III) and Co (IV) is considerably larger than that between two Co (III) atoms. The interaction of the above type is supposed to be applicable to the explanation of unusually deep colors in the crystals containing the same atoms in different oxidation states.

This work was supported in part by a grant from the Ministry of Education. Our thanks are offered to the analytical laboratory of our department for the absorption spectrum measurement of the aqueous solution.

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The Effect of Methyl Substitution on the Absorption Maxima of Quinoline Derivatives

By Kazuo SHIBATA and Takashi HOMMA

(Received July 4, 1952)

In 1947, Herzfeld[1] proposed a theory dealing with the effect of various kinds of substitutions on the position of the electronic absorption maxima of conjugated systems. According to his theory, the effect of substitution by the radicals containing two $2p\pi$ electrons as in the case of -Cl, $-NH_2$, -OH, etc. must always be bathochromic. Along the line of his reasoning, the effect of methyl substitution must be expected also to be more or less bathochromic, since the two bonding electrons between C and H will interact with the electrons of conjugated systems. In conformity with this expectation, there are extensive data showing that the absorption bands of $2p\pi$ electron systems are shifted redward by the effect of the methyl substitution.

In the course of our systematic study on spectroscopic properties of some conjugated systems, we have found, however, that some conjugated systems having quinoline nucleus represent exceptions to the above rule. The object of this paper is to present such examples and to describe some rule governing the effect of substitution on the position of absorption maxima of these compounds.

(1) K. F. Herzfeld, *Chem. Rev.*, **41**, 233 (1947).

Experimental

The compounds investigated were methyl derivatives of quinocyanines, tetrahydro-quinolines, benztetrahydro-quinolines and their picrates. Absorption spectra were measured by photoelectric method, with an Adam Hilger monochrometer. The solvent used was ethanol, and the thickness of the cell compartment was 1 cm.

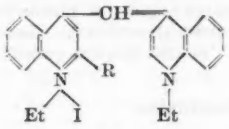
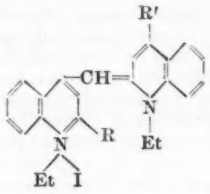
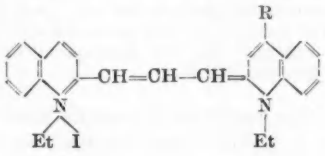
Results

The data obtained for quino-cyanines are listed in Table 1. As may be seen from this table, the substitution of methyl group in position 2 of quinoline nucleus shifts the absorption maxima redward, while the reverse is the case when the substitution is made at position 4. The absolute values of the shift caused by the substitution into position 2 are larger than those caused by the substitution in position 4.

With methyl derivatives of benztetrahydro-quinoline, we obtained the results given in Table 2. Since the methyl groups in positions 5, 6, 7 and 8 will not directly interact with the conjugated system, the effect of the substitution into these positions is expected to be less than the effect of the 2-, 3- and 4-substitutions. The data obtained confirmed this expectation. It may be remarked that the absorption maxima of 2-

Table 1

Absorption Maxima of Methyl Substituted Quino-cyanines

Compounds	R	R'	λ(Å.)	$\Delta\lambda$
	$-H$	—	5910	0
	$-CH_3$	—	5980	+70
	$-H$	$-H$	5580	0
	$-CH_3$	$-H$	5600	+20
	$-H$	$-CH_3$	5570	−10
	$-H$	—	6070	0
	$-CH_3$	—	6030	−40

methyl derivatives are situated at longer wavelengths than the maxima of 2,4-dimethyl derivatives.

In table 3, are shown the data obtained for the picrates of methyl substituted benztetrahydroquinolines. These compounds have two absorption bands, of which the one situated at longer wavelength is obviously due to the picric acid which is either in combined or in free state in the solution investigated. (See Table 3) In respect to the second absorption bands, the effects of methyl substitutions in various positions were found to follow virtually the same rule as was the case with benztetrahydro-quinolines.

These findings tell us that the same rule found for the absorption maxima of quino-cyanines may be applicable to benztetrahydro-quinolines and their picrates, and it may be that this behavior of the shift of absorption band by methyl substitution is the charateristic of the conjugated system having pyridine ring as a part.

In connection with the above data, it seems worthwhile to present the data of the melting points and the solubilities (%) in water of methyl derivatives of quinoline-iodoethylate. They are listed in Table 4, which shows that a rule analogous to the above mentioned one is found also in respect to these physical quantities; namely (1) the methyl substitution into position 2 enhances the melting point but lowers the solubility of quinoline-iodoethylate, while the substitution into position 4 shows the contrary effect, and (2) the

Table 2

Methyl Derivatives of Benztetrahydro-quinoline

Positions of methyl groups.	λ(Å.)	ε
2,7-	2840	18,000
2-	2800	16,000
2,4,6-	2800	13,000
2,4-	2760	14,000
none	2730	12,000
Pyridine	2550	9,000

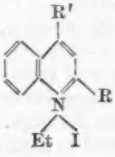
Table 3

The Picrates of Methyl Derivatives of Benztetrahydro-quinoline

Position of Methyl Groups	First Band (Å.)	Second Band (Å.)	ε (Second Band)
2,7-	3630	2810	21,000
2-	3630	3810	20,000
2,4-	3620	2780	21,000
None	3640	2730	14,000
8-	3630	2690	16,000
Picric Acid	3630	—	—

Table 4

Melting Points and Solubilities of Quinoline-iodoethylates

Compounds	R	R'	m.p.(°C.)	Solubility at 25°C.(%)
	$-H$	$-CH_3$	141	19.8
	$-H$	$-H$	156—157	8.1
	$-CH_3$	$-CH_3$	222—224	1.6
	$-CH_3$	$-H$	237—238	0.6

magnitude of the former effect is larger than that of the latter effect, as will be seen from the data of 2,4-dimethyl-quinoline.

In contrast to the cases described above, the effect of methyl substitution in tetrahydro-quinoline is always bathochromic as is shown in Table 5. This may be explicable if we realize that in these compounds the pyridine moiety in quinoline nucleus is saturated and, therefore, they may be regarded as alkyl derivatives of aniline from the viewpoint of conjugated system. In these compounds, the magnitude of bathochromic shift caused by methyl substitution is most pronounced in position 6, followed by 7 and then 8. It should also be remarked that the values of molar extinction coefficient ε of these compounds decrease with the shift of absorption maxima to longer wave-lengths, a phenomenon which is in quite reverse direction to that observed in the case of benztetrahydro-quinolines.

Table 5

Methyl Derivatives of Tetrahydro-quinoline

Positions of Methyl Groups.	λ(A.)	ε
2,6-	3100	1,100
2,4-	3040	1,600
2,4,6-	3030	800
2,7-	3030	1,900
2,4,7-	3000	1,300
7-	3000	1,600
8-	2990	2,000
2,4,8-	2950	2,600
2,8-	2920	3,000
Aniline	2840	—

Conclusion

The effect of methyl substitutions on the position of absorption maxima of some quinoline derivatives was investigated and it was found that there exists a certain empirical rule governing the relationship between the position of substitution and the shift of absorption band. Attention was called to the fact that in some quinoline derivatives the methyl substitution causes a hypsochromic shift of absorption band, a fact which is contrary to the expectation based on the now prevailing theory. The analysis of this phenomenon may be highly relevant from the standpoint of the theory of hyperconjugation.

The writers wish to express their earnest thanks to Prof. Eiji Ochiai and Mr. Yoshihisa Mizuno for the samples of quinoline derivatives used in the present investigation and also to Prof. Hiroshi Tamiya for his guidance and special interest in our study.

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An Equation of State in Analytical Form

By Tetsuya ISHIKAWA

(Received August 27, 1952)

In most of the text-books of physical chemistry which insert a table of van der Waals' constants a and b, no example of their actual evaluation is given, and students often fall into misconception that the constants are uniquely determinate from the original and its two derived equations at critical points. Concretely speaking, from these equations we obtain $b=V_c/3=RT_c/8p_c$ by substituting for V_c in the former from van der Waals' critical factor, $RT_c/p_cV_c=8/3$, and consequently $a=27p_cb^2=3p_cV_c^2=27(RT_c)^2/64p_c$, whereas for real gases, these two expressions of b give inconsistent values, $V_c/3$ being always less than $RT_c/8p_c$. The latter however has been accepted to make use of calculating molecular diameters.[1] To eliminate this inconsistency from van der Waals' equation, the following correction is needed:

$$b_{corr.}=b\left(\frac{3}{8}\frac{RT_c}{p_cV_c}\right)=\frac{V_c}{3}\left(\frac{3}{8}\frac{RT_c}{p_cV_c}\right)=\frac{RT_c}{8p_c},$$

where RT_c/p_cV_c in the correction factor is an actual critical factor, ranging from 3.23 to 3.97 for non-polar and larger slightly polar substances. Substitute $a_{corr.}$ for a corresponding to $b_{corr.}$, van der Waals' equation per mol. is

(1) e.g. Landolt-Börnstein I-1, 1950, p. 326.

Table 1

Validity of van der Waals' Equation for CO_2 at Several Isotherms ($p_c = 73.0$ atm.)

30.98°C. (critical temperature)		37.09°C.		41.95°C.		50°C.		100°C.		198°C.	
p(atm.)	f	p(atm.)	f	p(atm.)	f	p(atm.)	f	p(atm.)	f	p(atm.)	f
63.36	0.982	64.56	0.986	64.85	0.989	50	0.988	50	1.009	50	0.998
69.085	0.989	69.20	0.990	69.81	0.992	100	1.007	100	1.026	100	1.032
72.995	0.955	71.73	0.993	72.78	0.994	200	0.509	200	0.998	200	1.056
75.43	0.864	76.40	0.999	75.48	0.997	400	0.349	400	0.726	400	1.002
86.10	0.763	88.89	0.902	87.18	1.007	600	0.118	600	0.517	600	0.864
106.18	0.662	103.08	0.792	105.01	0.872	800	($V < b_{corr.}$)	800	0.337	800	0.760
138.65	0.568	136.01	0.655	134.85	0.731	1000	"	1000	0.161	950	0.619

Table 2

Ratios of the Molecular Association Degree to the Correction Factor for Critical Factor

Liquid	V(20°C.) cc.	$b_{corr.}$ cc.	RT_c/p_cV_c	α/β(20°C.)	$A/\frac{3}{8}\frac{RT_c}{p_cV_c}$
Br_2	51.23	58.56	3.46	17.66	0.969
Hg	14.81	17.04	3.40	46.29	1.025
CCl_4	96.45	126.6	3.68	11.51	1.029
CS_2	60.28	75.13	3.49	12.84	1.068
H_2O	18.04	30.49	4.46	3.92	(negative)
$CH_3CO_2C_2H_5$	97.89	141.0	3.95	13.27	1.040
C_2H_5OH	58.35	83.90	4.08	9.65	(1.100)
$C_2H_5OC_2H_5$	103.8	131.8	3.77	8.85	0.986
C_2H_5Br	75.16	84.31	3.14	11.64	1.046
CH_3COCH_3	73.43	86.90	3.02	11.44	(1.159)
C_6H_6	88.85	119.9	3.75	11.11	1.048
C_6H_5Cl	101.8	145.4	3.76	13.07	1.077
$CHCl_3$	80.18	99.42	3.44	12.80	1.046
C_7H_{16}	146.5	205.6	3.85	10.33	1.030
cyclo-C_6H_{14}	108.2	139.8	3.63	10.17	1.027
C_6H_{14}	130.6	174.7	3.80	9.00	1.011
CH_3OH	40.46	53.09	4.75	9.92	(0.927)
C_5H_{12}	162.7	236.1	3.86	11.18	1.052
C_5H_{12}	115.2	145.9	3.76	6.61	1.008
C_3H_7OH	74.74	110.0	3.99	9.80	(1.106)
$C_6H_5CH_3$	106.4	146.4	3.71	12.41	1.054

Table 3

($2-\varepsilon$) Values of Ne ($t_c = -228.7$°C, $p_c = 26.9$ atm., $d_c = 0.484$ g./cc)
$b = 13.90$, $\log a = 5.147154$, $\log V_0 = 4.350791$

−213.08°C		−208.10°C		−182.60°C		−141.22°C		−103.01°C		0.00°C	
p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$	p(atm.)	$2-\varepsilon$
23.086	1.946	24.071	1.950	32.067	1.973	33.840	1.996	35.558	2.011	22.064	2.093
24.810	1.946	28.844	1.952	32.988	1.973	37.707	1.998	36.697	2.006	23.555	2.078
26.673	1.946	31.948	1.952	36.438	1.976	38.581	1.998	40.610	2.022	25.867	2.107
29.365	1.946	37.856	1.953	36.880	1.977	43.319	2.006	42.107	2.021	28.468	2.115
32.441	1.947	41.798	1.953	41.371	1.977	49.881	2.004	55.136	2.026	30.790	2.118
37.418	1.947	58.472	1.954	42.533	1.981	51.916	2.004	58.583	2.030	39.753	2.059
53.896	1.948	64.451	1.955	49.943	1.981	66.471	2.019	78.110	2.059	44.892	2.072
59.769	1.948	69.692	1.955	50.514	1.980	78.558	2.029			59.777	2.076
66.271	1.948	74.532	1.955	63.320	1.983			mean	2.025	66.104	2.097
72.858	1.950	76.228	1.954			mean	2.007			74.059	2.122
79.698	1.950			mean	1.978					79.108	2.138
		mean	1.953							84.862	2.118
mean	1.947										
										mean	2.099

Table 4

$(2-\varepsilon)$ Values at Critical Points and Percentage Divergences of Approximate Formula $RT_c/p_cV_c=2/3\cdot(1+3V_c^{0.677})$ from Experimental Data

Substance	$2-\varepsilon$	Δ	Substance	$2-\varepsilon$	Δ	Substance	$2-\varepsilon$	Δ
He	1.931	+2.50	C_5H_{12}	1.924	+0.52	CH_3SH	1.922	−0.57
Ne	1.935	+2.35	i-C_5H_{12}	1.926	+1.55	C_2H_5SH	1.924	+0.85
A	1.925	+0.84	cyclo-C_6H_{14}	1.931	+3.95	CH_3SCH_3	1.920	−1.37
Kr	1.927	+1.63	C_6H_{14}	1.924	+0.53	$C_2H_5SC_2H_5$	1.933	+4.67
Xe	1.921	−0.89	C_7H_{16}	1.923	+0.28	HCO_2CH_3	1.905	−7.39
H_2	1.936	+4.31	C_8H_{18}	1.923	+0.78	$HCO_2C_2H_5$	1.913	−5.02
N_2	1.928	+1.93	Br_2	1.932	+3.51	$HCO_2C_3H_7$	1.917	−2.75
O_2	1.925	+0.83	Hg	1.915	−2.28	$CH_3CO_2CH_3$	1.909	−6.06
Cl_2	1.921	−0.79	CS_2	1.933	+4.42	$CH_3CO_2C_2H_5$	1.912	−4.82
CO	1.931	+3.01	CCl_4	1.927	+1.96	$CH_3CO_2C_3H_7$	1.914	−4.29
CO_2	1.918	−1.85	$CHCl_3$	1.940	+9.81	$CH_3CO_2CH_2CH(CH_3)_2$	1.937	+7.02
CF_2Cl_2	1.925	+0.96	CH_3OCH_3	1.918	−2.13	$C_2H_5CO_2CH_3$	1.913	−4.34
$COCl_2$	1.933	+4.31	$CH_3OC_2H_5$	1.922	−0.62	$C_2H_5CO_2C_2H_5$	1.915	−3.58
N_2O	1.908	−5.43	$C_2H_5OC_2H_5$	1.922	−0.57	$C_3H_7CO_2CH_3$	1.917	−2.82
PH_3	1.915	−3.13	$C_2H_5OC_3H_7$	1.926	+1.41	$(CH_3)_2CHCO_2CH_3$	1.912	−2.12
SO_2	1.908	−5.93	C_2H_5Cl	1.926	+1.16	$C_3H_7CO_2C_2H_5$	1.932	+4.63
$SnCl_4$	1.927	+2.06	$C_6H_5CH_3$	1.927	+1.87	$(CH_3)_2CHCO_2C_2H_5$	1.937	+7.08
CH_4	1.927	+1.64	C_6H_6	1.922	−0.49	$C_2H_5NH_2$	1.921	−0.82
C_2H_6	1.923	−0.12	C_6H_5F	1.920	−1.00	$(C_2H_5)_2NH$	1.922	−0.59
C_2H_4	1.927	+1.48	C_6H_5Cl	1.923	−0.02	$(C_2H_5)_3N$	1.934	+5.74
C_2H_2	1.915	−2.91	C_6H_5Br	1.921	−0.78	$(CH_3)_2CHCH(CH_3)_2$	1.926	+1.46
C_3H_8	1.921	−1.00	C_6H_5I	1.925	+1.01	$(CH_3)_2CHCH_2CH_2CH(CH_3)_2$	1.926	+1.57

The mean of $(2-\varepsilon)=1.923\pm0.008$, the mean of $\Delta=\pm2.6\%$.

written down:

$$p+\frac{a_{corr.}}{V^2}=\frac{RT}{V-b_{corr.}} \qquad (1).$$

The validity of equation (1) can be tested simply by calculating $f=(p+a_{corr.}/V^2)(V-b_{corr.})/RT$ at different isotherms, which must be unity, if the equation holds good. As seen from Table 1, f deviates from unity as pressure moves slightly away from the critical pressure, so that equation (1) is valid only within narrow limits of pressures, though the range becomes wider as the increase in temperature.

Moreover mere trial for the evaluation of values of $(V-b_{corr.})$ with ordinary liquids at an ordinary temperature proves that the applicability of equation (1) to liquids, should be rejected since all such values become negative (compare column 2 with column 3 in Table 2).

We have the pure thermodynamic equation

$$p+\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V=T\frac{\alpha}{\beta} \qquad (2),$$

where α and β denote thermal expansion coefficient and isothermal compressibility.(2) If there exists an equation of state for liquids, the thermal pressure of which has the form $ART/(AV-b_{corr.})$, A being a correction factor so as to let the denominator of thermal pressure of equation (1) be positive, the equality:

$$T\frac{\alpha}{\beta}=\frac{ART}{AV-b_{corr.}} \qquad (3)$$

may be satisfied, if A is suitably chosen. Since R (82.06 cc.-atm./deg. mol.) and V (cc./mol.) are both referred to 1 mol. of gases, A may be or may not be proportional to the degree of non-polar association at T°K.

For test of this postulation, 21 kinds of liquids have been adopted from Henning's table.(3) In Table 2 are given A's divided by $3RT_c/8p_cV_c$, from which we can conclude that A is in nearly the same magnitude with $3RT_c/8p_cV_c$, for ordinary liquids except acetone, alcohols and water, or in other words, for liquids having low dielectric constants relation (3) is transformed into

$$T\frac{\alpha}{\beta}=\frac{RT}{V-b} \qquad (4).$$

In accord with the above correction for thermal pressure, an appropriate correction for cohesive pressure will be considered below.

As already known b decreases as V decreases,

(2) e.g. International Critical Tables IV, p. 19.

(3) F. Henning's "Warmetechnische Richtwerte", p. 17-19, 20-21.

and so the assumption of keeping b to be constant independent of V must yield deviation in thermal pressure, but the deviation therefrom can be attributed to a suitable correction of a in cohesive pressure.

Now assume $a^*_{corr.}$ to vary slightly with V and take the following form:

$a^*_{corr.} = aV^{\varepsilon}$,
ε = a constant independent of pressure,

then for substances having low dielectric constants it follows from (1), (3) and (4) that

$$p + \frac{a}{V^{2-\varepsilon}} = \frac{RT}{V-b}, \qquad a = 3p_cV_c^2,\ b = V_c/3 \qquad (5).$$

Adopting pv- values of gases from I. C. T.[4] and Henning's table,[5] we have calculated $(2-\varepsilon)$ values for several gases. One of them is exampified in Table 3.

As a whole, the constancy of $(2-\varepsilon)$ values is fairly good over a wide range of pressures of each isotherm, though the constant range becomes restricted as the temperature decreases. The variation of $(2-\varepsilon)$ values with temperature is similar for all the examined gases except He, their values increasing from a value less than 1.92 to a value slightly greater than 2. Inserting the mean value of $(2-\varepsilon)$ at each isotherm in equation (5), we can obtain the equation of state at respective temperature. The thus analytically determinate equation is, therefore, more reasonable and accurate than a usual equation of algebraic form: $pV = a_0 + a_1/V + a_2/V^2 + a_3/V^3 + \cdots\cdots$.

Besides the gases above examined, all gases and liquids with known critical-point data except those having high dielectric constants take a universal value, 1.923 ± 0.008, for $(2-\varepsilon)$ at critical points (see Table 4).

The following are three formulae at the critical point which can be derived from the new equation of state.

The criteria generally used to determine whether or not any equation of state holds good are RT_c/p_cV_c, T_B/T_c (T_B = Boyle point) and $T_c/p_c \cdot (dp/dT)_c$. These are of course physico-chemical constants giving the values close to 3.7, 2.6 and 7.0 respectively but none of the proposed equations gives concordant values simultaneously.

Inserting $a = 3p_cV_c^2$ and $b = V_c/3$ in equation (5) at the critical point, and rearranging them, it follows that

$$\frac{RT_c}{p_cV_c} = \frac{2}{3}(1+3V_c^{\varepsilon}) \qquad (6),$$

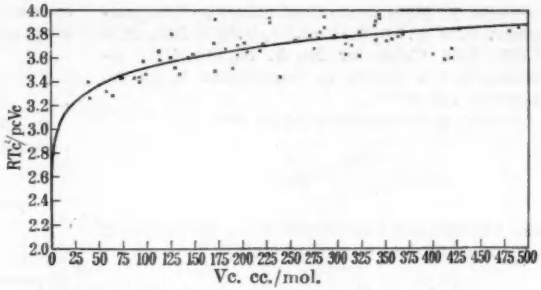

Fig. 1.—Relation between RT_c/p_cV_c and V_c for low dielectric substances.

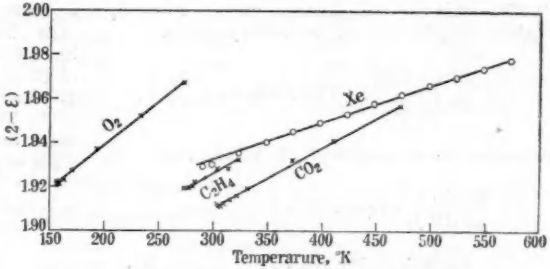

Fig. 2.—The temperature dependence of $(2-\varepsilon)$ for some gases.

here of course ε is its value at the critical point and V_c is expressed in cc.

Firstly, if we take the mean of ε from the results summarized in Table 4, relation (6) becomes

$$\frac{RT_c}{p_cV_c} = \frac{2}{3}(1+3V_c^{0.077}) \qquad (7),$$

which serves as an approximate formula. Δ's in Table 4 denote the percentage divergences from experiments and their mean value becomes ± 2.6 %. Also the relation between RT_c/p_cV_c and V_c is diagrammatically shown in Fig. 1, in which the curve is plotted by formula (7). Quite recently Himpan[6] put forward the empirical formula, $RT_c/p_cV_c = 2.92 + 1/3.\log(nM)$, where M is the molecular weight and n the degree of association, but its graphical test has shown that his formula is worse than formula (7).

Secondly, since the Boyle temperature is much higher than the critical temperature, relation $T_B = b/aR = 9p_cV_c/R$ derived from the van der Waals' equation may be allowable. Using this relation in conjunction with formula (7), there results

$$\frac{T_B}{T_c} = \frac{27}{2(1+3V_c^{0.077})} \qquad (8).$$

(4) International Critical Tables III, p. 4-19, 248-249.
(5) F. Henning, l.c., 34-40.
(6) J. Himpan, *Z. Physik*, **131**, 17 (1951).

Formula (8) gives concordant values with experiments: 2.70 (2.70), 2.60 (2.73), 2.58 (2.59), 2.57 (2.59), 2.56 (2.58) for Ne, A, N_2, CO, CH_4 respectively, the values in parentheses being the observed values.[7]

Thirdly, write equation (5) in the form

$$p=\frac{RT}{V-b}-\frac{a}{V^{2-\varepsilon}},$$

and differentiate with respect to T, remembering ε to be dependent on temperature,

$$\left(\frac{dp}{dT}\right)_V=\frac{R}{V-b}-\frac{a}{V^2}V^{\varepsilon}\log_e V\cdot\frac{d\varepsilon}{dT}.$$

Putting this in the thermodynamic relation, $(dp/dT)_c=[dp/dT)_V]_{T=T_c}$, we readily obtain

$$\frac{T_c}{p_c}\left(\frac{dp}{dT}\right)_c=\frac{3RT_c}{2p_cV_c}-3T_cV_c^{\varepsilon}\log_e V_c\cdot\left(\frac{d\varepsilon}{dT}\right)_c,$$

or replace from formula (7), it follows that

$$\frac{T_c}{p_c}\left(\frac{dp}{dT}\right)_c=1+3V_c^{0.677}-3\times 2.303T_cV_c^{0.677}\log_e V_c\left(\frac{d\varepsilon}{dT}\right)_c \qquad (9).$$

For example take CO_2 for which $T_c=304.2$°K., $V_c=44.01/0.460$ cc., $\varepsilon=0.082$ and $T_c/p_c\cdot(dp/dT)_c=7.14$[8] are given, $(d\varepsilon/dT)_c$ is evaluated to be -0.00029, or -0.00032 by the use of formula (9). These values agree well with the experimental value, $-(0.00028\pm0.0004)$, which has been obtained from the mean of $(2-\varepsilon)$ values at several isotherms: 1.912 (30.98°C., critical temperature), 1.916 (48.10°C.), 1.919 (57.75°C.), 1.935 (100°C.), 1.946 (137°C.), 1.969 (198°C.), 1.972 (258°C.).

As already stated, $3RT_c/8p_cV_c$ corresponds to the molecular association factor A at the critical point, so it follows from formula (6) that

$$A=(1+3V_c^{\varepsilon})/4$$

The numerical values of A lie from the lowest value of 1.22–1.29 for non-polar molecules such as Ne, He, A, Kr, N_2 and CO to the highest value of 1.47–1.49 for alkyl esters such as $CH_3CO_2CH_3$, $CH_3CO_2C_2H_5$ and $CH_3CO_2C_3H_7$. Although the former value, to whose class Br_2 and Hg belong, may be inconsistent with ordinary physicochemical knowledge of so-called normal liquids, yet it may be rather conceivable that non-polar association takes place at the critical point where gaseous and liquid states begin to coexist undoubtedly in a molecular aggregation different from the gaseous state, and that such association in the case of normal liquids may keep nearly constant for a wide range, from critical to ordinary temperatures.

Summary

(1) An equation of state in analytical form is proposed:

$$p+\frac{a}{V^{2-\varepsilon}}=\frac{RT}{V-b},\quad a=3p_cV_c^2,\quad b=V_c/3.$$

Values of $(2-\varepsilon)$ keep constant over a wide range of pressures of each isotherm. Taking the mean of $(2-\varepsilon)$ values at each isotherm, we obtain an equation of state which is more reasonable and accurate than the usual isothermal equation of algebraic form.

(2) Tests made with 66 kinds of substances having low dielectric constants prove that values of $(2-\varepsilon)$ at critical points are universal to give 1.923 ± 0.008.

(3) The following three formulae at the critical point are derived from the new equation in which V_c is expressed in cc./mol.

(i) $$\frac{RT_c}{p_cV_c}=\frac{2}{3}(1+3V_c^{0.677}),$$

(ii) $$\frac{T_B}{T_c}=\frac{27}{2(1+3V_c^{0.677})},$$

(iii) $$\frac{T_c}{p_c}\left(\frac{dp}{dT}\right)_c=1+3V_c^{0.677}-3\times 2.303T_cV_c^{0.677}\log V_c\cdot\left(\frac{d\varepsilon}{dT}\right)_c.$$

The first formula is concordant with $\pm2.6\%$ average divergence for 66 kinds of low dielectric substances and the two following are also equally concordant with the experimental data.

Addendum

The constancies of ε were found to be fairly good over a wide range of pressures at each isotherm. Their dependence on temperature, however, was left unsaid since there are but few favorable data from which a conclusion can be deduced.

Quite recently Beattie, Barriault and Brierley[1] reported on the compressibility measurements for gaseous xenon from the critical temperature to 300°C and over the density range of from 1 to 10 mol. per liter, and so by making use of their results we have had an opportunity to certify the linearity between ε and temperature which was already suggested in the case of CO_2.

For xenon we put $b=40.06$ cc. and $\log a=6.3993891$ calculated from their newly determined critical constants, $p_c=57.89$ atm., $d_c=8.32$ mol./liter, $T_c=16.65$°C.$+273.13$. The $(2-\varepsilon)$ values at every 50°C intervals from 25 to 275°C. are listed

(7) Adopted from E. A. Guggenheim's "Thermodynamics", p. 140.

(8) Adopted from S. Mizushima's "Physical Chemistry", III, p. 645.

(1) J. A. Beattie, R. J. Barriault, J. S. Brierley, *J. Chem. Phys.*, **19**, 1219 (1951).

Table 5

$(2-\varepsilon)$ for Xenon

mol./liter	$(2-\varepsilon)$					
	25°C.	75°C.	125°C.	175°C.	225°C.	275°C.
10.0	1.934	1.942	1.951	1.960	1.968	
9.0	1.935	1.942	1.951	1.959	1.968	1.977
8.0	1.934	1.942	1.951	1.959	1.967	1.976
7.0	1.932	1.941	1.950	1.958	1.967	1.975
6.0	1.930	1.940	1.949	1.957	1.966	1.974
5.0	1.928	1.939	1.948	1.957	1.965	1.973
4.0	1.926	1.938	1.947	1.956	1.964	1.972
3.0	1.926	1.937	1.947	1.955	1.963	1.971
2.0	1.927	1.938	1.948	1.956	1.964	1.972
1.0	1.931	1.942	1.951	1.959	1.966	1.974
Mean	1.930	1.940	1.949	1.958	1.966	1.974

Table 6

Percent Deviation from Experiments

mol./liter	$100\ (p_{calc.}-p_{obs.})/p_{obs.}$					
	25°C.	75°C.	125°C.	175°C.	225°C.	275°C.
8.0	−6.52	−1.66	−0.824	−0.396	−0.406	−0.473
7.0	−2.93	−1.35	−0.424	−0.073	−0.158	−0.164
6.0	−0.11	−0.10	−0.028	+0.163	+0.079	+0.024
5.0	+1.562	+0.525	+0.288	+0.377	+0.280	+0.213
4.0	+2.095	+0.805	+0.442	+0.493	+0.378	+0.328
3.0	+1.736	+0.724	+0.419	+0.443	+0.371	+0.321
2.0	+0.864	+0.346	+0.184	+0.259	+0.225	+0.205
1.0	−0.121	−0.162	−0.151	−0.034	−0.005	−0.011
Mean	1.99	0.709	0.345	0.258	0.228	0.217
(Beattie-Bridgeman's equation)	1.37	0.282	0.424	0.294	0.171	0.190

in Table 5, and the percent deviations, $100\ (p_{calc.}-p_{obs.})/p_{obs.}$, from 1 to 8 mol. per liter, in Table 6. As seen from these tables, the constancies of $(2-\varepsilon)$ at respective isotherms are quite satisfactory and the average percent deviations are as small as those of the Beattie-Bridgeman equation of state (the last line in Table 6).

The variation of $(2-\varepsilon)$ with temperature is diagrammatically shown in Fig. 2, in which are also plotted those of CO_2, C_2H_4 and O_2 which were computed from the compressibility data already mentioned.

As to xenon, $(2-\varepsilon)$ is strictly a straight line over the whole range of temperatures. This relationship appears to be equally well for the other gases as judged from their graphical representations. So that we can conclude that the linearity:

$$\varepsilon=\varepsilon_c+c(T-T_c),\ \varepsilon_c,\ c=\text{consts.}$$

holds true so far as the present data are concerned. Here ε_c is not ε at the critical point but the mean at the critical isotherm.

The author is indebted to SCAP CIE at Sasebo for having made him possible by mail from Tokyo to read the Journal of Chemical Physics, October, 1951, in which Beattie, Barriault and Brierley published their compressibility measurements for xenon.

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Rheology of Coal. II. Structure of Coal and Its Internal Viscosity at Audiofrequencies*

By Katsuya INOUYE

(Received July 7, 1952)

Introduction

Previous experiments on Young's moduli of coals by using a resonant frequency method[1] show that the elastic constant used as a measure of bond strength in solids describes the essential properties of coal in absolute units. A theory is proposed that coal is composed of independent molecules possessing similar crystallographic meaning and a more or less highly developed aromatic character, held together by van der Waals' forces of varying strength. These results also show that the experimental Young's moduli can be expressed by the equation,

$$E=E_0(1+K\phi) \qquad (1)$$

where, E=Young's modulus of the coal specimen, E_0=Young's modulus of "pure" coal molecules, ϕ=volume concentration of ash in the specimen, and K=a constant representing the degree of solvation. The values of E_0 and K are constants for each coal species and describe the properties of the coal. With a typical strongly-caking coal, the intermolecular forces would be expected to be small and at the same time the solvation of coal molecules by ash as skeleton should be most strong (see later). Furthermore, the physical meaning of the principal chemical theories for caking properties, i. e., the bitumen theory of F. Fischer et al.[2], or W. A. Bone and others[3] and also the gamma theory of R. V. Wheeler and his collaborators,[4] can be obtained from the Young's modulus measurements and a relationship between ash concentration and bitumen content. About the definition of caking, see Ref. 1.

If Equation 1 is valid, another linear function will exist between the internal viscosity and ϕ, because, theoretically Young's modulus and internal viscosity of solids containing "filler" show the same relationship respectively with filler volume concentration (Ref. 13 and 14). Also it may be possible to relate the phenomena of caking with viscosity measurements. With this in mind the experimental study measuring the internal viscosity at audiofrequencies by a vibration method were carried out.

Experimental

Although several experimental methods for measuring the dynamic properties of rubber-like solids[5] and tyre cord[6] have been described recently, they cannot be used with coal, because specimens of sufficient length are unobtainable and of differences in the rheological properties. Young's moduli of coal specimens can be measured with a crystal pick-up,[1] but this method is not adapted for the internal friction measurements, as the vibrational energy is characteristically dissipated by the Rochelle salt crystal. For the present purpose the author has constructed an apparatus as shown schematically in Fig. 1. The

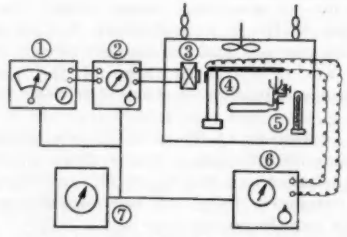

Fig. 1.—Experimental apparatus.
1. Oscillator 2. Amplifier 3. Magnet
4. Sample and Pick-up 5. Thermo-regulator
6. Amplifier 7. Voltage Stabilizer

* Presented at the Colloid Chemistry Symposium, Nov., 1950.

(1) K. Inouye, *J. Colloid Sci.*, **6**, 190, (1951).

(2) F. Fischer et al., *Brennstoff-Chem.*, **5**, 299, (1924), **6**, 33, (1925).

(3) W. A. Bone et al., *Proc. Roy. Soc. (London)*, **A 105**, 608, (1924); *Trans. J. Soc. Chem. Ind.*, **44**, 291 T, (1925).

(4) R. V. Wheeler et al., *Trans. J. Soc. Chem. Ind.* **103**, 1704, (1913), **109**, 707, (1916).

(5) S. D. Gehman, D. E. Woodford and R. B. Stambaugh, *Ind. Eng. Chem.* **33**, 1032, (1941); J. H. Dillon, I. B. Prettyman and G. L. Hall, *J. Appl. Phys.*, **15**, 309, (1944); A. W. Nolle, *J. Appl. Phys.*, **19**, 753, (1948); R. S. Witte, B. A. Mrowca and E. Guth, *J. Appl. Phys.*, **20**, 4881, (1949).

(6) W. J. Lyons and I. B. Prettyman, *J. Appl. Phys.*, **18**, 586, (1947).

Table 1

Descriptions of Samples

Sample	Origin	Classification	Caking Property	Volatile Matter, Mean Value (dry, ash-free basis)
American	U. S. A.	Bituminous	Strongly caking	35
Takashima	Kyushu, Japan	Bituminous	Strongly caking	38
Toro	Saghalien, U. S. S. R.	Bituminous	Weakly caking	46
Yubetsu	Hokkaido, Japan	Producer gas coal	Non-caking	64
Shosaku	China	Anthracite	Non-caking	7.7

calibrated audiofrequency oscillator sends alternating current from 50 to 10,000 c./sec. to the coil of an electromagnet through a power amplifier of 3.2 watt. Vibration of specimen with magnet and light iron plate cemented on the specimen opposite to the magnet is detected by "U-effect" of a capillary pick-up, and leads to the voltage amplifier of 55 decibels. The "U-effect" was recently discovered by S. Ueda and coworkers,[7] and is the electric voltage produced by mechanical vibration of a capillary within which are many mercury and electrolyte drops arranged alternately. The capillary pick-up used in these experiments has a length of several cm and diameter of approx. 0.4 mm., weighs about 0.1 g. including the leads and contains approx. 30 drops of mercury and 30 drops of 1N. H_2SO_4. The pick-up is cemented with bakelite cement to the top of the specimen. The specimen under examination is contained in a thermostat, regulated to 0.05°C., the thermostat being suspended by ropes and rubber cords in order to remove floor vibration.

The assembly of the supporter is important and it is found best to bury one end of the specimen in Portland cement clamping it carefully after the cement has solidified. All parts of the apparatus should be carefully shielded, the out-put of the amplifier being kept constant to avoid induction effect. The errors due to the additional mass at the top of the specimen and to the damping by air were considered to be sufficiently small to avoid consideration.

The specimens were shaped from coal blocks to the form of a rectangular bar with an accuracy of 1% in each dimension, using motor grinder and sandpaper or by grinding on a glass plate with carborundum. All specimens were cut parallel to the bedding plane.

The differential equation of the vibration of bar is assumed after K. Sezawa[8] as below,

$$\rho\frac{\partial^2 y}{\partial t^2}+E\kappa^2\frac{\partial^4 y}{\partial x^4}+\eta\kappa^2\frac{\partial^5 y}{\partial t\partial x^4}+\xi\frac{\partial y}{\partial t}=0 \quad (2),$$

where, ρ = density of the sample, E = Young's modulus, η = coefficient of viscosity, κ = radius of gyration of cross section, and ξ = coefficient of friction by air. Resolving the above equation assuming the clamped-free bar vibration, E and η can be calculated[9] approximately as,

$$E=\frac{4\pi^2\rho n^2 l^4}{\kappa^2 m^4} \quad (3), \text{ and}$$

$$\eta=\frac{2\lambda n\rho l^4}{\kappa^2 m^4} \quad (4),$$

where, n = resonant frequency, l = length of the specimen, m = a factor corresponding to the mode of vibration, and λ = logarithmic decrement. If the amplitude (out-put voltage of the pick-up) is plotted as a function of the frequency, the familiar resonance curve is obtained. Taking the half value breadth of the curve as Δn, the logarithmic decrement, λ, can be easily calculated according the theory of damping vibration in the first approximation as,

$$\lambda=\frac{\pi}{\sqrt{3}}\frac{\Delta n}{n} \quad (5).$$

From Equation 4 and 5, η can be calculated from the measurable values of n, Δn, ρ, l and the thickness of specimen. Using small specimens of coal, only the first fundamental mode of vibration can be detected, so "m" is always 1.875.

Results and Discussions

Filler Effect of Ash.—The internal viscosity values were obtained using specimens with various ash contents of five typical coals, as shown in Table 1.

The rectangular bar specimen was at first set in another apparatus for measuring the Young's modulus from the fundamental flexural resonant frequency,[1] and then, as previously described, buried in the Portland cement, set in the thermostat of 30.0°C. and the resonance curve was measured repeatedly until constant values of n and Δn were obtained. Thus the Young's modulus calculated by Equation 3 from the clamped-free vibration was compared with the value calculated from the flexural vibration method to check the correct mode of vibration, as the flexural vibration method has better accuracy. The results for the Young's modulus are in Reference 1. As

(7) S. Ueda, F. Tsuji and M. Watanabe, *Bull. Inst. Chem. Research, Kyoto Univ., Japan*, **18**, 108, (1949), **19**, 44, (1949), **20**, 28, (1950).

(8) K. Sezawa, *Rep. Aeronautical Res. Ins. Tokyo Univ., Japan*, No. 45, (1928).

(9) K. Sezawa and K. Kubo, *J. Appl. Phys. Japan*, **1**, 1, (1932); Y. Tani, *J. Appl. Phys. Japan*, **9**, 372, (1940).

described in a later section, the damping properties of coal are markedly influenced by the resonant frequency, so η was measured at about 1400 c./sec. by adjusting the dimensions of the specimen. Some dependence of η on moisture is supposed, but on this point no information was obtained from this apparatus.

The relation between η and ϕ, calculated under the assumption that the density of ash is 2.0, and that of pure coal is 1.2, is shown in Fig. 2.

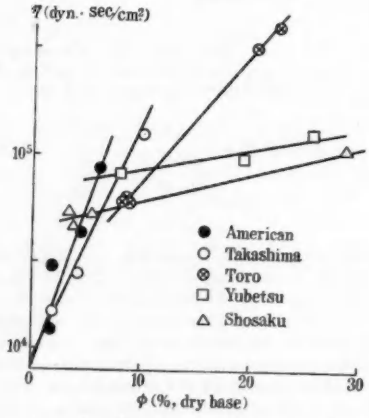

Fig. 2.—Internal viscosity and ash volume percentage.

It is noteworthy, as proposed in the introduction, that η is a linear function of ϕ,

$$\eta = \eta_0(1 + K'\phi) \qquad (6),$$

where, η_0 = internal viscosity of pure coal, and K' = a factor representing the solvation of coal molecules with ash. Relation of the same form as Equation 6 has been proved theoretically on dilute suspension by A. Einstein,[10] E. Guth and R. Simha,[11] W. Kuhn[12] and others, and also on solid with filler by E. Guth and O. Gold[13] and E. Guth.[14]

Table 2

Values of η_0 and K'

Sample	η_0 dyn. sec. cm.$^{-2}$	K'	E_0 dyn. cm.$^{-2}$	K
American	1×10^5	16	1.8×10^{10}	38×10^{-2}
Takashima	3×10^5	3.5	2.0×10^{10}	20×10^{-2}
Toro	2.3×10^4	2.7×10^{-1}	3.6×10^{10}	7×10^{-2}
Yubetsu	8.4×10^4	1.0×10^{-2}	4.5×10^{10}	13×10^{-2}
Shosaku	6.8×10^4	1.3×10^{-2}	7.0×10^{10}	-2×10^{-2}

(10) A. Einstein, *Ann. Phys.*, **19**, 289, (1906); **34**, 591, (1911).
(11) E. Guth and R. Simha, *Kolloid-Z.*, **74**, 147, (1936).
(12) W. Kuhn, *Kolloid-Z.*, **62**, 269, (1933); **68**, 2, (1934).
(13) E. Guth and O. Gold, *Phys. Rev.*, **53**, 322, (1938).
(14) E. Guth, *J. Appl. Phys.*, **16**, 20, (1945).

Table 2 describes two constants η_0 and K' characteristic to each coal as well as E_0 and K in Equation 1 from Reference 1. The magnitude of E_0 and η_0 and also of two "solvation factors" K and K' change in the same order, and this fact appears to support the theory and the ash skeleton models of coal structure as illustrated in Reference 1.

The caking properties of coal correspond naturally to the weakness of intermolecular forces as well as strong solvation with inorganic ash portion, namely the molecules of the caking coal become mobile at some elevated temperatures for their weak attraction and thermal stability, by the plasticizer effect of the nonsolvated molecules, in contrast to the non-caking coal molecules which decompose before such plastic condition is accomplished because of their too strong intermolecular forces.

Plasticizer Effect of Bitumen.—The bitumen is the fraction of coal molecules held together with weak van der Waals' forces so as to be extracted by benzene at 300°C. in an autoclave. The points of the chemical theories of caking properties have been that the bitumen is necessary to the caking coal[2] and that its relative relationship to residual parts is important.[3]

The author has shown[1] a relation between ϕ and bitumen content B (in %, dry, ash-free base) applicable to all bituminous coals, i. e.,

$$\phi = \frac{7.5\times10^3}{B^2} \qquad (7).$$

Substituting ϕ of Equation 6 by ϕ of Equation 7, a relation between η and B is obtained. Thus using the values of η_0 and K', η can be calculated for corresponding experimental B values. Table 3 shows calculated viscosity values compared with the measured values.

The bitumen content was determined on the same specimens previously used for measuring the internal viscosity. The specimen was powdered to pass 60 Tyler mesh sieve, dried one hour at 105°C., weighed, and five grams of the sample and 100 cc. of pure benzene were put in an autoclave. The autoclave was shaken automatically throughout the extraction, heated electrically up to 300°C. in 2.5 hours and retained at this temperature for 3 hours. The pressure was about 50 atmospheres. The extracted sample was washed with benzene in a Soxlet apparatus and then dried. The bitumen content was calculated from the difference of ash contents between the original and this extracted sample, assuming that no ash was moved into the bitumen. Fig. 3 shows the relationship between B and experimental η values.

As the relation between Young's modulus and B,[1] these results suggest the physical meaning of chemical bitumen theories, namely on one hand the plasticizer effect of bitumen molecules remarkably reduces the rheological values and on the other hand, perhaps, the importance of relative nature with residue. For instance, Toro (weakly caking) coal has lower bitumen content

Table 3

Calculated and Experimental Viscosity

Sample	η_0 dyn. sec. cm^{-2}	K'	B, %	η_{calc}	$\eta_{exp.}$
American	1×10^5	17	36.67	9.6×10^4	9.4×10^4
			55.63	4.2×10^4	4.8×10^4
			70.00	2.7×10^4	1.9×10^4
Takashima	3×10^5	3.5	24.30	1.4×10^5	1.1×10^5
			35.72	6.5×10^4	4.5×10^4
			50.53	3.4×10^4	2.7×10^4
Toro	2.3×10^4	2.7×10^{-1}	8.77	6.3×10^5	1.5×10^5
			15.63	2.1×10^5	8.0×10^4
			21.37	1.2×10^5	7.8×10^4
			32.60	6.7×10^4	7.8×10^4

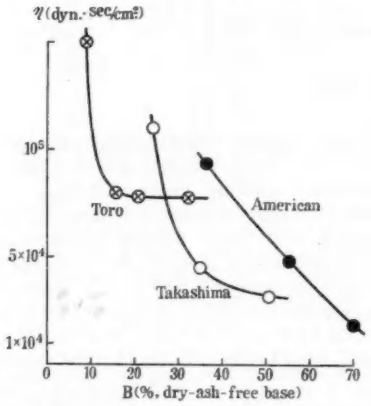

Fig. 3.—Internal viscosity and bitumen content

even in its saturation state, at higher viscosity values, in other words, the bitumen in this coal is less effective as plasticizer, and it is suggested that improvement of the relation between bitumen and residue (or, of some inner condition) is necessary, before the coal is used as better caking coal.

Dependence of Frequency and Temperature.—To elucidate the dependence of internal viscosity on frequency, three typical specimens of American strongly-caking coal, Yubetsu producer gas coal and Shosaku anthracite were selected, the dimensions of which were large enough at first for taking η values of the same specimens at various resonant frequencies by changing the dimensions occasionally. Such measurements were carried out at 30.0, 45.0, 60.0 and 70.0°C. The measurable frequency range was from ca. 400 to 950 c./sec. Detailed values are ommitted from this paper for the limitation of approved space of this Bulletin.*

At each temperature, E and η decrease with increasing frequency. At any given frequency, η of the strongly-caking coal decreases more markedly with increasing temperature, than of the producer gas coal and the anthracite. E does not decidedly change within this range of temperature.

There is at present no theoretical basis, using a relaxation distribution function, to interpret this dispersion. However, at least qualitatively, the decrease of η of the caking coal even in such low temperature range seems to be interesting as to characterize its rheological properties. Taking η values of the American coal for four different temperatures at 600 c./sec. on the graphs, an activation energy is about 1 kcal./mol., calculated by the Andrade formula,[15]

$$\eta = Ae^{U/RT} \qquad (8),$$

where, U = Activation energy of viscosity, T = Absolute temperature, R = Gas constant, and $A = a$ constant. It may be interesting to note that the activation energy of viscosity is slightly lower than the energy of thermal motion, RT, at caking temperature, say ca. 1.4 Kcal./mol. at 450°C., provided the activation energy is constant up to such high temperatures.

Although the author has to state that much theoretical and experimental work should be carried out before further detailed discussions can be done, he suggests that the caking properties are due chiefly to the remarkable decrease of friction in the viscosity element, with low activation energy, instead of thermal stability of *intra*micellar conditions, i. e., the whole system, when the temperature is elevated, fuses and swells by low viscosity of bitumen (or, more freely combined) molecules as plasticizer when the micells, in which the molecules are more strongly combined by the solvation forces with ash portion, exist presumably unchanged. This condition is expected to be accomplished more easily than when all molecules in the system have to become mobile.

The author acknowledges with sincere thanks the enthusiastic assistance of Hideo Tani, and

* The results are given in the Reports of the Fuel Research Institute, No. 60, Nov., 1952

(15) E. N. Andrade, *Nature*, **125**, 580, (1930).

Mitsuo Abiko during the investigation. He is also indebted to Dr. T. Shimmura, Dr. M. Kurokawa and Mr. A. Baba (this Institute) for their interest in this work. Thanks are expressed to Dr. H. Marsh (King's College, Univ. of Durham) for revising the manuscript.

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Studies of Crystalline Hydrates. II. Thermal Transition and Dehydration of Ni-, Fe-, Co-, Zn-, Mn-, and Mg-sulfate Hydrates

By Hideaki CHIHARA and Syûzô SEKI

(Received June 28, 1952)

Introduction

The studies of the dehydration of crystal hydrates are of basic significance for clarifying the nature of the interaction between water and various materials on one side, and the mechanism of the typical hetero-phase reaction involving solids on another side, particularly in the cases in which atomic structures of the crystals are accurately known. Although numerous investigations have been made on the solubility of the hydrates for their successive degrees of hydration,(1) on the dissociation pressures and on the decomposition-reaction mechanisms,(2) there still remain much to be investigated from their atomistic and energetic points of view. Recently, the magnetic susceptibility measurement of hydrates containing paramagnetic ions and the nuclear magnetic resonance absorption studies of the crystal water have interested the physicists.(3) In these respects, it would be desirable to study the dehydration processes and the behavior of water molecules in hydrates in greater detail.

Although the method of the thermal analysis has been used by many investigators for the study of dehydration process, the detailed experiment in relation to the crystal structure, as far as the authors are aware, is only that of copper sulfate pentahydrate measured by Taylor and Klug.(4) We have applied the differential thermal analysis further to Ni sulfate hydrate, typical of known crystal structure, and other related hydrates under various conditions in order to elucidate their dehydration processes and also whether or not these crystals undergo transitions similar to those of $CuSO_4 \cdot 5H_2O$ which are considered to be attributed to the rotation of water molecules.

Experimental

Materials.—$NiSO_4 \cdot 7H_2O$.—The product of Kahlbaum Co. was recrystallized from an aqueous solution at about 0°C. and the excess water in the precipitate was removed by pressing it between filter paper and then dried in a desiccator containing the same hydrate partially dehydrated as a desiccating material. This procedure of drying was adopted for all of the samples mentioned below.

$ZnSO_4 \cdot 7H_2O$.—The product of Kahlbaum Co. was recrystallized from aqueous solution at about 0°C.

$MgSO_4 \cdot 7H_2O$.—The product of Merck Co. was recrystallized from aqueous solution at about 0°C.

$FeSO_4 \cdot 7H_2O$.—The product (extra pure) of Katayama Co. was recrystallized from slightly acidic solution at about 0°C.

$CoSO_4 \cdot 7H_2O$.—The product (extra pure) of Ishizu Co. was recrystallized from aqueous solution at about 0°C.

$MnSO_4 \cdot 7H_2O$.—The product (extra pure) of Ishizu Co. was recrystallized from an aqueous solution at about 0°C.

$NiSO_4 \cdot 6H_2O$.—The hexahydrate was prepared either by crystallizing from an aqueous solution

(1) N. V. Tanzov, *J. Russian Phys.-Chem. Soc.* **55**, 335 (1924); A. Chretien and R. Rohmer, *Compt. rend.* **198**, 92 (1934); H. H. Ting and W. L. McCabe, *Ind. Eng. Chem.* **26**, 1207 (1934); R. Rohmer, *Compt. rend.* **210**, 669 (1940); J. H. Krepelka and B. Rejha, *Coll. Czechoslovak. Chem. Com.* **5**, 67 (1933); F. Fraenckel. *Z. anorg. Chem.* **55**, 223 (1939).

(2) "Chemical Reactions involving Solids", Discussions of the Faraday Society, 1938; E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.* **41**, 488 (1945).

(3) J. Wheatley and D. Halliday, *Phys. Rev.* **75**, 1412 (1949); G. E. Pake, *J. Chem. Phys.* **16**, 327 (1948).

(4) T. I. Taylor and H. P. Klug. *J. Chem. Phys.* **4**, 601 (1936).

at about 40°C. or dehydrating the heptahydrate. All these samples were stored in the desiccators during various periods of time to examine the aging effect.

Apparatus and Procedures.—The apparatus used for the differential thermal analysis was the same as that previously reported,[5] so a brief comment may be given here. As shown in Fig. 1, A is a copper block with two drilled holes, in

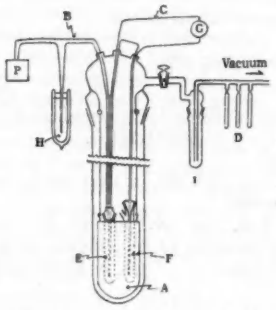

Fig. 1.—A schematic diagram of the apparatus for differential thermal analysis.
E: a reference cell containing NaCl;
F: a sample tube; G: a galvanometer;
H: the standard temperature (ice);
I: a liquid air trap; P: a potentiometer.

each of which a thinwalled glass tube is fitted: one contains NaCl as a standard material and the other the sample to be investigated. B and C are copper-constantan thermo-couples for the measurements of temperature of NaCl and of temperature difference between the sample and NaCl, respectively. In order to determine the water content of the samples, the capillary tubes D are used for collecting water vapor produced by decomposition. The water content at successive stages of dehydration is measured by the following procedure. After the completion of a stage of dehydration which is shown by the restoration of increased temperature difference to its normal steady state value, the heater is turned off and the cell system is pumped off slowly to condense the dehydrated water in a liquid air trap I. The temperature difference between the sample and NaCl is again on the increase by the self-cooling of the sample due to the evaporation of liberated water. As the amount of liberated water in the sample tube decreases, the deflection of the galvanometer for the differential thermocouple stops increasing and then begins to decrease. As soon as this decrease turns to increase again on account of the beginning of the next step of dehydration, the pumping is stopped and dry air is introduced into the whole system to prevent further dehydration. The collected water is then led

(5) I. Nitta, S. Seki, and H. Chihara, *J. Chem. Soc. Japan, Pure Chem. Sect.* **70**, 387 (1949).

Table 1

Determination of Water Content of Nickel Sulfate Hydrates

Initial wt.	Loss of wt. at the transition or dehydration points.		
Room temp.	86°	110°	132°
0.829 g.	0.009 g.	0.115 g.	0.160 g.
	Loss of water. mole/mole of $NiSO_4$		
	≈0	2.09≈2	2.82≈3

to one of the capillary tubes D and the amount of water is weighed after the tube is fused off. As an example, data for $NiSO_4 \cdot 6H_2O$ are given in Table 1. In every run, the sample was heated at a constant rate of 0.6 to 1.5°C. per minute under atmospheric pressure, unless otherwise stated. The X-ray powder photographs were taken by copper Kα radiation. To examine the structure change at the transition temperature, a high-temperature camera was employed.

Experimental Results.—(1) **Differential thermal analysis:**

One of the typical temperature-time curves is illustrated in Fig. 2. The whole results under different conditions for various samples are given in Figs. 3 to 8 in which the positions of the vertical lines represent the dehydration or transition temperatures and their length means an approximate value of the heat effect. The diffuse band stands for a transition or a dehydration ranging over a temperature interval. The downward band is for the evolution of heat. Ordinates show the temperature scale in t°C. (Fig. 2 corresponds to Fig. 3c). Dotted vertical lines show

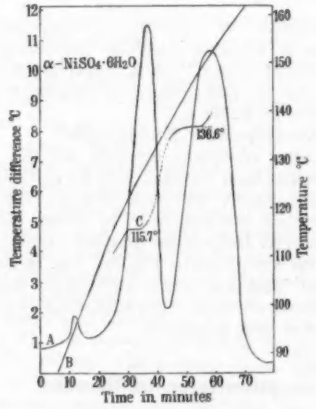

Fig. 2.—An example of differential thermal analysis.
A: Temperature difference between the sample and NaCl. (left scale)
B: Heating curve of NaCl. (right scale)
C: Heating curve of the sample which is drawn by subtracting A from B. (right scale).

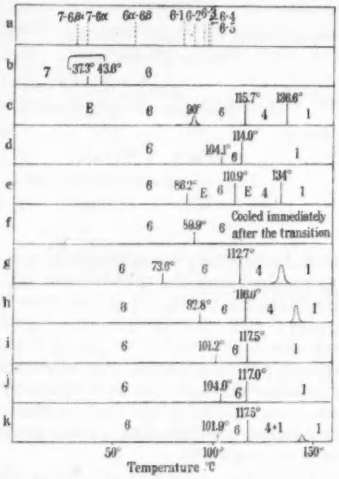

Fig. 3.—Differential thermal analyses of nickel sulfate hydrates. "E" stands for evacuation and admission of dry air. Time of storage of samples is as follows:
(b) 80 d. As to the two peaks, see in the text.
(c) 1 d. Continuation of (b).
(d, e, f) 13.5 m.
(g) Continuation of (f).
(h) 25 d. A week after grinding.
(i) 3.5 m. Immediately after grinding.
(j) 6 m. Unground sample.
(k) 6.5 m. Coarsely crushed sample.
(e, f, g, h) and (i, j, k) are two groups of specimens, each being parts of the same samples, respectively. d. = days, m. = months.

the transition or dehydration temperatures of hydrates in aqueous solutions determined from the solubility curves.[1] Fig. 3e corresponds to the experiment for determining the degrees of hydration given in Table 1.

(2) **X-ray powder photographs:**

Since the complete analysis of the crystal structure has been reported only for α-$NiSO_4 \cdot 6H_2O$ and $NiSO_4 \cdot 7H_2O$, we have applied the X-ray identification method only to these materials. The observed Debye line diagrams under various conditions are given in Fig. 9. Fig. 9e shows the reference positions calculated from the known crystal structure data of α-$NiSO_4 \cdot 6H_2O$ determined by Beevers and Lipson.[6]

Discussion of Results

(a) Comparison of the dehydration temperatures determined from the differential thermal analysis with those from the solubility curves.

It should be noted that the dehydration and the transition temperatures determined by these two methods have, in general, different meanings,

(6) C. A. Beevers and H. Lipson, *Z. Krist.* **83**, 123 (1932).

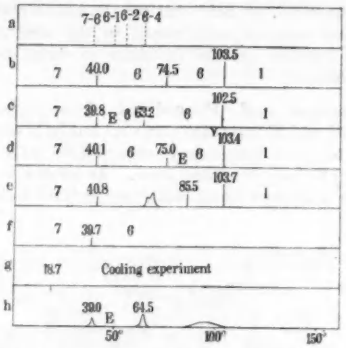

Fig. 4.—Differential thermal analysis of $ZnSO \cdot 7H_2O$.
(b) 15 m.
(c) 16.5 m. At 98°, a heat evolution is observed.
(d) 18.5 m. (e) 30.5 m. (f) 30.5 m.
(g) Continuation of (f). Cooling curve.
(h) Continuation of (g), A month after (g).

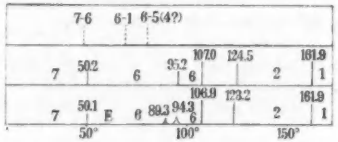

Fig. 5.—Differential thermal analysis of $MgSO_4 \cdot 7H_2O$.

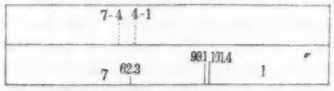

Fig. 6.—Differential thermal analysis of $FeSO_4 \cdot 7H_2O$.

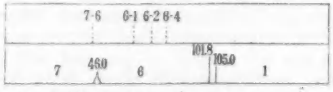

Fig. 7.—Differential thermal analysis of $CoSO_4 \cdot 7H_2O$.

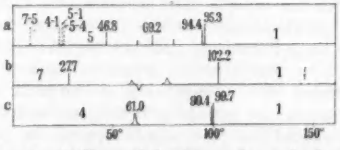

Fig. 8.—Differential thermal analysis of $MnSO_4$ hydrates.
a) Pentahydrate, b) Heptahydrate,
c) Tetrahydrate.

i. e. the material subjected to the thermal analysis belongs to an open system, so that the existing phases are not absolutely in their equilibrium state, whereas in an aqueous solution the various phases in contact are in the true equilibrium state. Taking this situation into account, comparisons are now made of the transition temperatures in Figs. 3 to 8. In the case of Mn sulfate, none of the dehydration temperatures in the present study coincides with those obtained from the solubility curve, but in other hydrates the first step of dehydration (7→6) nearly agrees in both methods and this is particularly confirmed with Ni sulfate, in which case the dehydration temperature (43.6°C.) in the first run is shifted to lower temperature (37.3°C.) in the next repeated run, the second one being in perfect agreement with the dehydration temperature (heptahydrate→β-hexahydrate) in the aqueous solution (Fig. 3b). The solubility curve of hexahydrate, when temperature is raised, intersects with that of monohydrate first and then those of di-, tri-, tetra-, and penta-hydrates successively if they can exist. Hence, the lower hydrates are more stable than the higher ones in the aqueous systems (see, for instance, Fig. 3a). However, the situation is entirely different in an open system.* In raising temperature, the hexahydrates are dehydrated to form lower hydrates in just the opposite order from that in the open system. And none of the dehydration temperatures coincides in these two processes of dehydration. In aqueous solutions, the stable modification of nickel sulfate between 31.5 and 60°C. is the α-hexahydrate (6α), and it is this modification that first appears in the dehydration of the heptahydrate in the aqueous system. But in the dry system, as is shown in Fig. 3b, the transition from the heptahydrate to β-hexahydrate (6β) does take place first, which is evident by the coincidence of the dehydration temperatures in the dry and the wet systems at 37.3°C. A possible explanation of this apparent coincidence may be that a small amount of liberated liquid water causes a more or less similar situation to the wet system although the transformation to 6α from 6β is not admitted on account of the slow velocity of its nucleation. The fact that the unstable β-phase appears first is already reported by Simon and Knauer[7] and is also ascertained by our X-ray photographs. This fact, together with the phenomenon that the unstable dehydration products appear in reverse order in comparison with the result obtained from the solubility studies, may be explained by the so-called "rule of successive transformation[8]."

(b) **Dehydration stages and the phase transitions without accompanying dehydration.**

As mentioned above, prior to its first dehydration, $CuSO_4 5H_2O$ undergoes phase transitions which may be attributed to the rotation of water molecules according to Taylor and Klug.[4] As expected, similar transitions were found in the present investigation in some of the hydrates examined. The present discussion, with reference to its dehydration process, will be mainly concerned with the case of nickel sulfate which was studied in greatest detail. The β-form of hexahydrate produced by the first decomposition of heptahydrate changes spontaneously and slowly to 6α and circumstantially to tetrahydrate, so that the product initially obtained by heating heptahydrate, consisting of a mixture of 6β and heptahydrate, changes to a mixture of 6β, 6α and tetrahydrate even at a constant temperature as the decomposition proceeds. Fig. 9a corresponds to the mixture of heptahydrate and 6β containing possibly minute amount of 6α. Fig. 9c contains no heptahydrate and consists of 6β and a trace of 6α, while Fig. 9b consists mainly of 6α and a small amount of 6β. Thus, these three figures are considered to represent the main features of the successively transformed products of the heptahydrate, respectively. Although there remains a possibility that the last two figures contain traces of tetrahydrate, it was not ascertained on account of the difficulty of taking a Debye photograph of pure tetrahydrate. Further heating of the hexahydrate leads to a phase

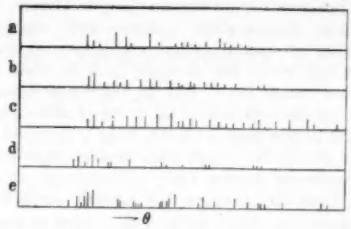

Fig. 9.—Debye photographs of nickel sulfate hydrates.

a) heptahydrate, b) α-hexahydrate,
c) β-hexahydrate (green part of the specimen formed by the dehydration of the heptahydrate),
d) γ-hexahydrate at 100°C. (Fig. 3h),
e) α-hexahydrate (Ref. 6).

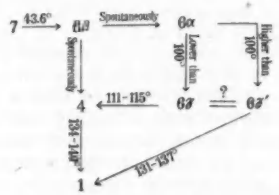

Fig. 10.—A schematic diagram correlating various modifications of nickel sulfate hydrates.

* It may be noticed that water produced in the first step of dehydration would dissolve a part of the hexahydrate, and lower hydrate than hexahydrate would be present before the second step of dehydration takes place.

(7) A. Simon and H. Knauer, *Z. anorg. allg. Chem.* **242**, 375 (1939).

(8) R. S. Bradley, *Quarterly Rev.* **5**, 323 (1951).

transition accompanying no dehydration.* This transition temperature varies very sensitively depending on the external conditions as well as on the history of the sample; that is, these temperatures range from 70.5 to 117°C. as shown in Fig. 3. Althongh a similar state of affairs is also reported in the case of $CuSO_4 \cdot 5H_2O$, detailed conditions governing it are not clearly described.[4] It is confirmed by the Debye photograph at about 100°C. that 6α changes its crystal structure at the transition point (Fig. 9 d). And it was also found that this transition is completely reversible by both the X-ray method and the differential thermal analysis (Fig. 3 f, g). It is interesting to note here that when 6α was coarsely crushed or was stored long (longer than a few months), the transition temperature is always a few degrees higher than 100°C. and on top of that the stage of tetrahydrate does not appear (see Fig. 3 d, i, j). On the other hand, the sample, finely powdered or not stored long, undergoes transition at a lower temperature and always goes through the stage of tetrahydrate (see Fig. 3 c, e, g, h). In Fig. 3 k, is given the intermediate case between these two. The reason for such behavior is not yet clear, but it is very plausible to assume that a trace of tetrahydrate which may be present after grinding or short-time storing acts as a self-catalyst for the growth of the phase of tetrahydrate. Fig. 10 illustrates schematically the various phases of nickel sulfate hydrates, in which 6γ (or $6\gamma'$) denotes the phase found by the present study which is formed by the transition below (or above) 100°C. These two phases, 6γ and $6\gamma'$, may be identical with each other although there is no direct proof about it.*

In the cases of other hydrates, phase transitions without dehydration were also found at 62—85° for $ZnSO_4$, 89—95° for $MgSO_4$, and 60—85° for $MnSO_4$. In every case, these temperatures are sensitively influenced by the external conditions and the sample's history similarly to that of Ni salt. These results together with the dehydration stages are given in Figs. 4 to 8. It is of interest to note that there exists the dihydrate of magnesium sulfate which has hitherto been unknown at least in an open system. In all cases the final stages of hydration at the highest temperature examined are monohydrates.

(c) **Effect of evacuation, heat evolution, rehydration and aging effect.**

The effect of evacuation was also examined upon the dehydration and transition temperatures as well as upon the velocity of transition from an amorphous to a crystalline state. Generally, the temperature of dehydration is not so influenced by this treatment as the transition temperature. The heat evolution effect, which may be due to transformation of an amorphous, unstable, skeleton formed after dehydration to stable crystalline state, has recently been remarked by several investigators in the cases of $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot 4H_2O$ by Khomyakov,[9] Mn-oxalate dihydrate by Volmer and Seydel,[10] and $ZnSO_4 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ by Frost, et al.[11] Similar effects have been found in the present investigation in $ZnSO_4 \cdot 7H_2O$ at about 100°C. and in $MnSO_4 \cdot 7H_2O$ at about 65°C., the latter of which occurs even without previous evacuation (Fig. 8 b). It may be worthwhile to note that in the case of $ZnSO_4 \cdot 7H_2O$ the effect of evacuation which gives rise to evolution of heat is revealed at the temperature just below the second dehydration point after the transition (63.2°C.) is over, prior to which it has been evacuated (see Fig. 4 c).* Finally, a brief comment may be given on the experiment of rehydration for $ZnSO_4 \cdot 7H_2O$. When this substance is heated up to about 40°C. and then cooled, the evolution of heat is observed, which is attributed to the rehydration (Fig. 4 f, g). This may be explained either by the reaction

$$ZnSO_4 \cdot 6H_2O + H_2O = ZnSO_4 \cdot 7H_2O$$

or by the reaction

$$6(ZnSO_4 \cdot 6H_2O) = 5(ZnSO_4 \cdot 7H_2O) + ZnSO_4 \cdot H_2O$$

which can be predicted from the measurements of dissociation pressures.[12] The authors are for the latter interpretation since repeated heating and cooling procedure across this dehydration point results in the dehydration of more than one mole of water per mole of the heptahydrate (Fig. 4 h). The aging effect due to storing the sample for a long time is very complicated. Although, to date, no definite conclusion can be drawn about it, it may be said that the transition temperatures are much more influenced than the dehydration temperatures.

The authors wish to express their grateful thanks to professor Nitta for his encouragement and valuable suggestions during this work. The cost of this research has been defrayed from the funds of Taniguchi Kôgyô Shôreikai as well as from the Scientific Research Encouragement Grant from the Ministry of Education to which the authors' thanks are due.

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* The evidence of no dehydration at the transition point is given in Table 1.

** The shift of the transition temperature of Fig. 3 j to Fig. 3 k and the simultaneous appearance of the small hump indicating the existence of the tetrahydrate may be regarded as a proof of this identity.

(9) K. C. Khomyakov, *J. Phys. Chem.* (*U. S. S. R.*) **11**, 805 (1938).

(10) M. Volmer and G. Seydel, *Z. physik. Chem.* A **179**, 153 (1936).

(11) G. B. Frost, K. A. Moon and E. H. Tompkins, *Can. J. Chem.* **29**, 604 (1951).

(12) L. C. Copeland and O. A. Short, *J. Am. Chem. Soc.* **62**, 3285 (1940); See also R. E. Barieau and W. E. Gisuque, ibid. **72**, 5676 (1950).

* It is known that in the case of $ZnSO_4 \cdot 6H_2O$ the velocity of transformation from amophous to crystalline state depends on the water vapor pressnre and has a maximum around pressure of 0.95 mm.Hg (Ref. 11).

Analysis of High Molecular Substances by Chromatography. I. Paper Chromatography of Polyethylene Oxide

By Sanshiro KUME, Tai YAMAMOTO, Kiyoteru OTOZAI, and Shouzow FUKUSHIMA

(Recived July 28, 1952)

Introduction

Studies of the molecular weight distribution of a variety of high polymers, which would be highly interesting, are at present impracticable because of the limitations and tediousness of conventional fractionation procedures. The recent success of paper chromatography in the separation of closely related chemical species in the fields of the organic and inorganic chemistry and the brilliant result of chromatographic "frontal analysis" of high polymers by S. Claesson,[1] together with its defects, have directed our attention to the possibility of applying paper chromatography to the analysis and fractionation of high polymers, referring to the case of partition chromatogaphy of nitrocellulose suggested by M. C. Brooks and R. M. Badger.[2]

The principal difficulties encountered in chromatography of high polymers are supposed to be: (1) difficulty in detection of the chromatograms, because polymers have in general neither color nor color reaction, (2) difficulty in the development under the condition of equilibrium of the solute between the fixed and mobile phases, because the velocity of establishing the equilibrium of high polymers is in general very slow compared with the ordinary flow rate of the developing solvent, (3) difficulty in preventing the unexpected disturbance of the solvent flow, which makes the chromatographic separation imperfect, especially in case of high polymers consisting of the continuous homologues. Overcoming these difficulties mentioned above, S. Claesson has first succeeded in the adsorption chromatography of polymers employing the frotal analysis of Tiselius. The results obtained, however have some defects related to the chromatography of adsorption type and especially to frontal analysis of homologues. That is, there is no determinate means to know whether the distribution in molecular weights is the only factor which dominates the distribution of polymer species suggested by the chromatograms obtained and the method, although very useful for analytical purposes, seems unavailable for fractionating purposes of polymers.

We have chosen polyethylene oxide of relatively low molecular weight as the first example of the hydrophilic polymers, and investigated the chromatographic separation with the use of the usual technique of paper chromatography. The difficulties and defects mentioned above have been overcome by a new technique of color development of polyethylene oxide, the selection of a suitable developing solvent, and the general features of paper chromatography.

Experiment

(A) Sample: Commercial polyethylene oxide, "carbowax 1,000", "carbowax 4,000" and "carbowax 6,000" of Carbide and Carbon Chemicals Corp. without special purification were used as the fractionated polyethylene oxide samples, which have the general properties as shown in Table 1.

Table 1

Properties of Carbowaxes

Name	Freezing Rrange (°C.)	Solubility in Water (% by weight)
Carbowax 1,000	35—40	70
〃 4,000	50—55	62
〃 6,000	58—62	50

Before the preparation of the sample solutions the crushed samples were dried for seven days ("1,000") and three days ("4,000" and "6,000") in a desiccator over calcium chloride to constant weights because they are somewhat hygroscopic.

(B) Development: With the use of micropipette 0.5 μl. of 2% aqueous solution of carbowax was put in the diameter of 3-5 mm. on filter paper strip (Toyo Roshi No. 3, for the quantitative analysis, 45 cm.×1 cm.), which beforehand has been dried for one day in a desiccator over calcium chloride in order to hold the constant amount of adsorbed water and to make the developed spot sharper. The position of the original

(1) S. Claesson, *Arkiv Kem. Mineral. Geol.*, **26 A**, No. 24, 1 (1949).
(2) M. C. Brooks and R. M. Badger, *J. Am. Chem. Soc.*, **72**, 1705 (1950).

spot was 8 cm above the surface of the developing solvent when set up in the apparatus, at which the flow rate of the solvent becomes stationary. Six strips were placed in a desiccator over calcium chloride until the original spot dried up and set up in the apparatus[3] as shown in Fig. 1, which was held in the thermostatt of

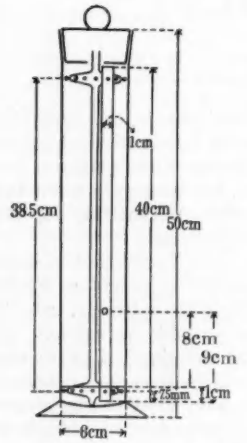

Fig. 1.—Apparatus for development.

25±0.1°C, and developed upwards with solvent for 4-6 hrs. making the distance between the solvent front and the position of the original spot 12-15 cm. The longer time interval between the putting of the sample on the paper and the development has a tendency to leave more parts of the sample of higher molecular weight at the original point.

(C) Color development: The strips developed were dried in room atmosphere, sprayed with 1/30% ethanolic solution of fluorescein, and dried

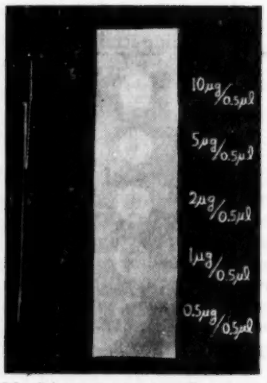

Fig. 2.—Limiting amount and concentration of detection.

(3) cf. K. Otozai, *J. Japan. Chem.*, **4**, 411 (1950).

naturally again. The presence of polyethylene oxide on the paper was detected as a white spot on a yellow background. The limiting amount and concentration of detection of this method were approximately 0.5 μg. polyethylene oxide per 0.5 μl water, as shown in Fig. 2. This value, however, was affected by the amount of impurity in the paper, which may cause some interference in the yellow color development of fluorescein on the paper.

Results and Discussions

The developing solvent benzene-chloroform system was at first employed, which has been investigated by G. V. Schultz et al.[4] as the solvent useful for the partition fractionation of polyethylene oxide, water being used as the parent solvent. Because of the lack of affinity with the paper, however, this solvent was not suitable for the developing solvent in paper chromatography. Among various solvents involving butanol as the principal component the butanol-ethanol-water system was found to be the most suitable for the paper chromatography of polyethylene oxide. The R_f values obtained with the use of this solvent are given in Table 2, in the case of the single samples. The symbol x corresponds to the concentration of ethanol in a mixture consisting of 100 parts of butanol, 100 parts of water and x parts of ethanol in volume. The upper

Table 2

R_f Values of Single Samples

x	$(R_f \pm \Delta R_f) \times 100$		
	Carbowax 1,000	Carbowax 4,000	Carbowax 6,000
0	22±0(22)	3±0(9)	0±0(4)
5	28±0(20)	2±0(6)	0±0(4)
10	38±0(22)	5±0(8)	0±0(4)
15	42±1(15)	7±0(10)	0±0(4)
20	50±1(16)	9±0(11)	0±0(6)
25	58±1(16)	17±0(13)	0±0(5)
30	63±2(14)	33±1(14)	6±1(10)
35	67±2(8)	46±2(8)	25±2(10)
40	76±2(10)	56±2(9)	36±2(8)
50	77±1(6)	71±2(5)	59±1(5)
60	77±1(8)	73±2(6)	66±2(6)
70	77±1(7)	76±3(5)	74±2(5)

layer was taken for developing in case the system separates into two layers at 25±0.1°C. The system consists completely of one phase for x values larger than 40. The R_f values are calculated as

$$R_f = (l_1 + l_2)/2l \quad \text{(cf. Fig. 3)}$$

(4) G. V. Schultz and E. Nordt, *J. prakt. Chem.*, **155**, 115 (1940).

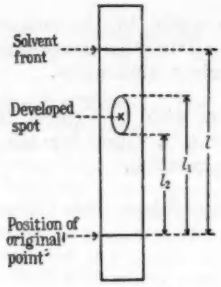

Fig. 3.

and the numerical values in brackets represent the values calculated as $(l_1-l_2)/2l$, the latter of which would correlate to the proper divergence of the spot during chromatography and the distribution of the molecular weight of polyethylene oxide used. These figures are the mean values in several experiments.

The relations between R_f values of single samples and the concentrations of ethanol in the solvent are given in Fig. 4. Furthermore the values in Fig. 4 were rearranged in Fig. 5, in which the values of the average molecular weight M of each sample were obtained by the viscosity measurement of aqueous solutions at 20±0.01°C, using the K_m constant 1.8×10^{-4} for 0.5% solution.[4]

From the form of the curves in Fig. 5 the most suitable solvent for the separation of three samples is that of $x=35$, because this solvent gives approximately linear and steep curve. A demonstration of the practical separation of the three samples by the use of this solvent is shown in Fig. 6 together with the individual developments of single samples for comparison, and R_f values obtained were shown in Table 3. which represent the good independency of each sample in paper chromatography.

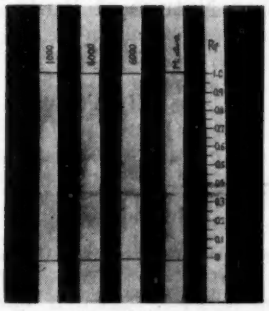

Fig. 6.—Separation of three components.

Table 3

Comparison of R_f Values of Single and Mixed Samples

$(R_f \pm \Delta R_f)\times100$

	Carbowax 1,000	Carbowax 4,000	Carbowax 6,000
Single	67±2(8)	46±2(8)	25±2(10)
Mixed	68±3(9)	45±3(7)	28±3(7)

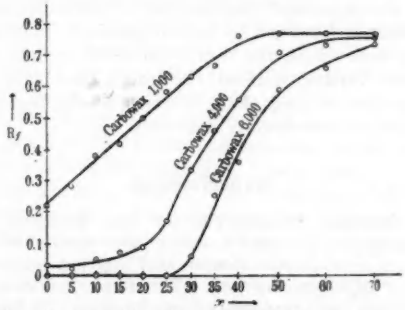

Fig. 4.—Relations between R_f and concentration of ethanol.

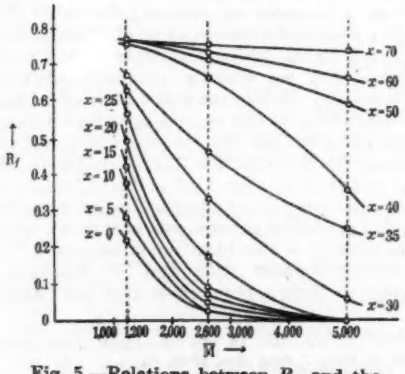

Fig. 5.—Relations between R_f and the average molecular weight.

Using the curve ($x=35$) in Fig. 5 as a working curve one can readily determine the average molecular weight of polyethylene oxide, although it is only relative, in the range of 1,000-5,000, where the molecular weight is determined only with difficulty by every known method at present. Thus employing paper chromatography a new simple relative method of determination of the average molecular weight, and a possibility of a simple method of determination of distribution function, and finally a possibility of fractionation of hydrophilic polymers have been proposed, using polyethylene oxide of molecular weight 1,000-5,000 as an illustration.

Summary

(1) It was found that polyethylene oxide on paper can readily be recognized with fluorescein as an adsorption indicator.

(2) It was found that paper chromatography can be applied also for polyethylene oxide in the range of the average molecular weight 1,000-5,000, as the first case for hydrophilic polymer, in the same manner as low molecular weight substances.

(3) It was found that paper chromatography gives a simple new relative method of determination of the average molecular weight of polyethylene oxide in the range mentioned above, where all the other conventional methods encounter serious diffiiculties.

The authors wish to express their sincere thanks to Prof. T. Titani for his encouragement of this research.

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On the Nature of Built-Up Film. III. Effect of Dissolved Anion on Mono- and Multilayers of Octadecylamine

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(Received August 14, 1952)

Introduction

In the preceding papers[1],[2] the effects of metallic ions on the built-up film of stearic acid were reported. There it was suggested that some metallic ions, e. g., copper, aluminum or thorium, are adsorbed from an aqueous solution in their characteristic *p*H range as a fairly large and complex unit. This suggestion is in agreement with the experiments of Matuura and one of the present authors,[3],[4] who have arrived at the same conclusion based upon the remarkable expansion and rigidity exhibited by the monolayer of fatty acid spread on an aqueous solution containing the ions mentioned above. A certain wetting phenomena can also be explained from the same point of view which was reported by Inaba[5] of our laboratory. Wolstenholme and Schulman[6],[7] obtained the similar experimental results and explained these phenomena from a different point of view

The fact[2] that the intensity of water-repellency of metal stearate built-up film, after the treatment with or without aqueous salt solution, is parallel to the presumed complexity or macromolecular structure of the film, seems to suggest a profound effect for the wettability of the easiness of overturning of the molecules which is hindered by two-dimensional molecular network in the film. To confirm this, we have further studied the interaction between the film of long chain amine and the organic anion of the known structure.

Experimental

Material. — Octadecylamine was prepared by reduction[8] of nitrile which was synthesized[9] from Merck's pure stearic acid and was purified by distillation in vacuo. The final product was recrystallized repeatedly from benzene. Its melting point was 83~84°C. Bigelow, Glass and Zisman[10] however obtained the free amine of melting point ranging from 51.5 to 52.5°C., and amine bicarbonate of melting point being about 80°C., while the Beilstein value of the former was reported to be 53°C. This leads us to the conclusion that we actually obtained the amine bicarbonate. In fact, the result of micro nitrogen determination of this sample agreed with theoretical value for the bicarbonate within an error ($N_{obs.}$, 4.37%; $N_{calc.}$ for $C_{18}H_{37}NH_2 \cdot H_2CO_3$, 4.23 %, whilst $N_{calc.}$ for $C_{18}H_{37}NH_2$, 5.21%). The molecular area of octadecylamine in monolayer spread on water surface was calculated, taking into account of this bicarbonate formation.

Dibasic organic acids were of Takeda's or Riedel de Haën's pure grade and recrystallized

(1) M. Muramatsu and T. Sasaki, This Bulletin, **25**, 21 (1952).
(2) M. Muramatsu and T. Sasaki, This Bulletin, **25**, 25 (1952).
(3) T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951).
(4) R. Matuura, This Bulletin, **24**, 277 (1951).
(5) A. Inaba, This Bulletin, **25**, 174 (1952).
(6) G. A. Wolstenholme and J. H. Schulman, *Trans. Faraday Soc.*, **46**, 475 (1950); **47**, 788 (1951).
(7) G. A. Wolstenholme and J. H. Schulman, *Trans. Faraday Soc.*, **46**, 498 (1950).
(8) F. Kraft, *Ber.*, **15**. 1728 (1883); N. K. Adam and J. W. W. Dyer, *J. Chem. Soc.*, **1925**, 72.
(9) H. Stephen, *J. Chem. Soc.*, **1925**, 1875.
(10) W. C. Bigelow, E. Glass and W. A. Zisman, *J. Colloid Sci.*, **2**, 563 (1947).

several times. A highly purified sample of sodium alginate was given by Mr. S. Miyamoto of our laboratory.

Apparatus and Method.—The surface pressure of monolayer was measured by the Wilhelmy balance modified by one of the authors of this paper.[11] The monolayers were deposited onto the metal slide by either of the two methods, namely by the ordinary Langmuir-Blodgett technique[12] and by the special method of using benzene solution of amine as a piston oil placed near the slide, the details of which were reported in the preceding paper.[2] Optical thickness of built-up films was determined by means of the interference method as used in the preceding reports.[1],[2] The experimental error associated with the apparatus was ±1.5 A. All experiments were carried out at room temperature from 7 to 14°C.

Results

Monolayers Spread on the Surface of Distilled Water.—The pressure ~ area curve of the amine monolayer spread on the surface of distilled water proved to be of a typical condensed film. The cross-sectional area of molecules at zero compression lies in the range of 21.7—25.6 A.²/molecule depending upon various factors. It seems to be characteristic for this film that the reproducibility is poor presumably due to its sensitivity towards pH,[13] or to the presence of carbon dioxide[10] in water, and also due to the aging of the film.[14] Moreover, it was observed thet the shape of curve was profoundly affected by velocity of compression, as reported by Marsden and Schulman,[15] and Hoffman, Boyd and Ralston,[16] though the other conditions were the same. The similar result was reported in the case of the monolayer of antifoaming agent.[17]

Deposition of Multilayers from Water Surface.—By use of the Langmuir-Blodgett technique[12] attempts were made to build multilayers of free base from the surface of water, pH of which was adjusted to larger than 5, to prevent the formation of ammonium salt.[14] Under the pressure of tricresyl phosphate, castor oil and oleic acid as piston oils, through all pH region, the monolayer did not adhere to a bare surface of stainless steel slide both for down- or up-trip. On the other hand, it could be deposited onto the barium stearate base as successive Y-multilayers when the substrate pH was smaller than 10 and each double layer was sufficiently dry after withdrawal. Under the piston pressure of tricresyl phosphate, the films of 4—6 layers showed an optically perfect homogeneity when they were deposited from the substrate water of pH 5—8.6. However, in the case of the film exceeding six layers, optical contrast of the echelon became weak indicating the heterogeneity of the film, which was seen already in the first double layer when pH of substrate water was 8.6—10. Using castor oil or oleic acid as a piston oil, on the other hand, an optically homogeneous film could be obtained only up to 2—4 layers when it was built from substrate water of pH 5—6, while heterogeneous film resulted in the other range of pH. In the case of homogeneous film, the spacings in multilayer were found between 24.0—25.3 A. (24.5 A. for the mean value of twelve experiments) per layer irrespective of the conditions of building-up. It should be noted that remarkable fogging occurred in the built-up films of amine when more than about ten layers were deposited. Similar results were reported in the cases of the films of long chain esters[18] and phthiocerol.[19]

At pH>10, the films were deposited as X-layer independent of the piston pressure. The slide was withdrawn from the solution completely wetted with water but it quickly peeled back soon after.

Interaction of Amine Monolayer with Organic Anions in the Underlying Solution.—In Fig. 1 are shown the effects of some dibasic organic acids and sodium alginate dissolved in a substrate water, on the pressure~ area curve of the amine monolayer. The solutes were dissolved to 10^{-4} mol./l. for acids and 0.1% for sodium alginate, and pH of the substrate was kept to 4.5—5.0. The same result was also obtained when the oxalic or succinic acid was injected in water beneath the monolayer. It was seen, in general, that the monolayer expanded with increasing distance between the polar groups in each anion of the substrate. The curve of sodium alginate, in this connection, lies between succinic and

(11) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941).
(12) K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 964 (1937).
(13) C. G. Lyons and E. K. Rideal, *Proc. Roy. Soc. London*, **A 124**, 333 (1929).
(14) N. K. Adam, *Proc. Roy. Soc. London*, **A 126**, 526 (1930).
(15) J. Marsden and J. H. Schulman, *Trans. Faraday Soc.*, **34**, 748 (1938).
(16) E. J. Hoffman, G. E. Boyd and A. W. Ralston, *J. Am. Chem. Soc.*, **64**, 498 (1942).
(17) A. L. Jacoby and C. E. Johnson, *J. Phys. Colloid Chem.*, **53**, 1417 (1949).
(18) E. Stenhagen, *Trans. Faraday Soc.*, **34**, 1328 (1938); G. Knott, J. H. Schulman and A. F. Wells, *Proc. Roy. Soc. London*, **A 176**, 534 (1940).
(19) S. Ställberg and E. Stenhagen, *J. Biol. Chem.*, **143**, 171 (1942).

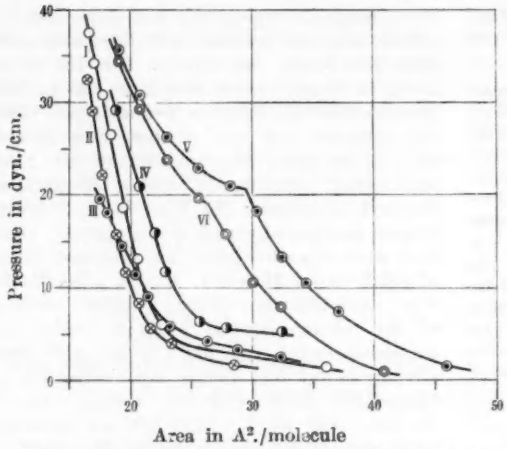

Fig. 1.—Pressure~area curve of octadecylamine monolayer spread on various substrate: I, distilled water; II, oxalic acid; III, malonic acid; VI, succinic acid; V, adipic acid; VI, Na alginate.

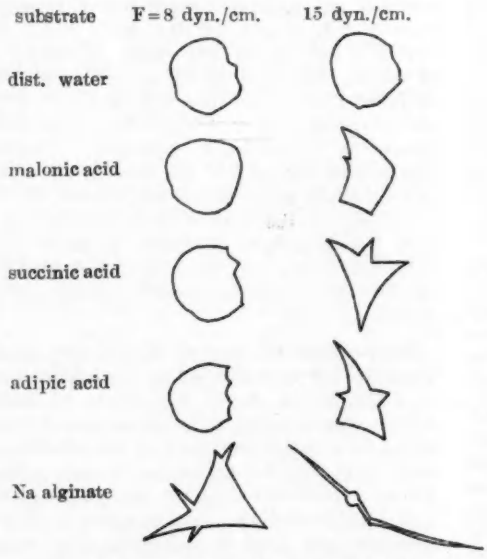

Fig. 2.—Expansion pattern of octadecylamine monolayer.

adipic acids. With respect to the mechanical properties, however, sodium alginate behaved remarkably different from the other anions. It rendered the amine monolayer highly rigid, while such an effect was not so remarkable in the case of dibasic acids. This behavior is shown in Fig. 2, in which the expansion patterns of camelia oil[4] are schematically illustrated for different solute and surface pressure.

Multilayers of Amine Built Up from the Surface of Organic Anion Solution. — The monolayer of amine formed on the surface of the solution as described above could easily be deposited onto the barium stearate echelon, excepting the case of sodium alginate, as successive Y-layers which showed an optical homogeneity up to six layers. On the other hand, X-film alone was obtained in the case of adipic acid, and this film was so patchy indicating the incomplete deposition that we could not measure its spacing. The opticallv perfect film was obtained by the method of deposition as described in the preceding report.[2] It was confirmed with dibasic acids except for adipic acid, that the thickness of a monolayer is unaffected by the method of deposition.

Table 1 shows the apparent spacing of these films under the piston pressure (15 dyn./cm.) of castor oil, together with

Table 1

Cross-sectional Area of Molecules and Apparent Spacing in Built-up Film

Substrate Solution	Apparent Spacing per Layer in A.	Cross-sectional Area in A.²/molecule
distilled water	24.5	20.0
$(COOH)_2$	34.7	19.1
$CH_2(COOH)_2$	32.5	19.1
$(CH_2)_2(COOH)_2$	32.6	22.1
$(CH_2)_4(COOH)_2$	20.9	31.2

the cross-sectional area of a molecule at the same pressure. All these films, especially those built up from the solutions of organic ions, proved to have an extremely hydrophobic property, as well as a strong resistance against corrosion and dissolution in contrast with the built-up film of stearic acid.[20],[1] Thus the film transferred from the aqueous oxalic acid substrate, for instance, showed no change in the film thickness as well as the water-repellent property, even when it was soaked in distilled water for a long time (44 hrs. or more). It is a very interesting fact that it became wettable towards water, when it was immersed in the sodium alginate solution. The minimum time of immersion necessary for wetting is shown in Table 2. In this table, the case of KH_2PO_4 (buffered to $pH=7.2$ with

(20) J. J. Bikerman, *Proc. Roy. Soc. London*, **A 170**, 130 (1939).

Table 2

Minimum Time of Immersion in Aqueous Sodium Alginate(0.1%) Required to Wet Built-Up Film Transferred from Various Aqueous Substrate

Aqueous Substrate	Time of Immersion in min.
distilled water	1-3
$(COOH)_2$	7
$CH_2(COOH)_2$	10
$(CH_2)_2(COOH)_2$	15
$(CH_2)_4(COOH)_2$	25
KH_2PO_4	∞

NaOH) was listed in addition to the cases of dibasic acids. Amine monolayer spread on this substrate was as rigid as that spread on the alginate, and it could be transferred onto the slide but was extremely heterogeneous.

Discussion

Easiness of Building-Up of Amine Film. —There are several experimental evidences that the affinity between the metal surface, e. g., platinum,[10] silver or copper surface,[7] and long chain amine when the molecules of free amine were adsorbed from non polar solvent, is as strong as that between metal and long chain acid. Then, it seems to be a contradiction that the monolayers of free base spread on water do not adhere, as was mentioned already, to the bare surface of metal. This may be explained by the stronger affinity of amine molecules towards water surface, than towards nonpolar solvent. However when the echelon of barium stearate was dipped into water carrying the monolayer, it took up the amine molecules as an A-layer, its polar group orienting towards bulk water. On withdrawal, moderately strong anchorage of amine molecules to echelon by non polar group and to the next amine layer by polar group enables the formation of AB-double layer. This interaction can reasonably by assumed from the following facts. A strong cohesion of long chain amine was predicted from the formation of islands in the monolayer[13] and from the lower value[21] of c. m. c. of long chain amine than that of the corresponding anionic soap. Also in our experiments the heterogeneity or the fogging in the film may presumably be an indication of the tendency of transformation into the three-dimensional microcrystal which may be a more stable form than the two-dimensional one. That the homogeneous thicker film could only be obtained using the lower piston pressure, and that the successive layer could be better transferred onto the echelon from the surface of aqueous substrate containing organic acid than from that without acid, may be considered to have some relation to this phenomenon.

Surface Interactions between Amine and Organic Anions. — In Fig. 1 a somewhat distinct condensation was observed for amine oxalate film* compared with the case of free base, while, for amine malonate, pressure~area curve at low pressure was nearly the same as the control test, and a remarkable expansion was seen with succinate and adipate. It is probable that the cross-sectional area of molecules in monolayer is chiefly affected by the distance between carboxyl groups in substrate anion, to which amine molecules in monolayer are considered to attach. Thus in the film of, say, amine adipate, octadecyl radicals attach separately to the carboxyl groups of adipate ion under low pressure. This idea is also supported by the decrease in apparent spacing shown in Table 1, which can be interpreted to be the increase in distance of octadecyl radicals in the film as was already pointed out[2] referring to the metal stearate. We may also find Schulman's strong polar and weak van der Waals' type interaction[22] in the behavior at a high pressure region. On the other hand condensation of amine oxalate would be accounted for by the attachment of the amine monolayer to carboxyl groups which are located closely in the acid molecules.

The effects of dissolved alginate ion upon the mono- and multilayers of amine are of very great interest. It can be pointed out from Figs. 1 and 2, and is also expected from X-ray data[23] on alginate solution, that the distance between ionic groups in the alginate ion is slightly smaller than between groups in adipate, and that a large number of polar groups in anion interact with amine molecules. This interaction renders the film highly rigid. Such a type of interaction was called multiple-point polar association by Cockbain and Schulman.[22] The remarkable rigidity due to the interaction of this type has also been shown by several investigators for amine film on

(21) A. W. Ralston, C. W. Hoerr and E. J. Hoffman, *J. Am. Chem. Soc.*, **64**, 97 (1942); **68**, 2460 (1946); I. M. Kolthoff and W. Stricks, *J. Phys. Colloid Chem.*, **52**, 915 (1948); M. Nakagaki, *J. Chem. Soc. Japan*, **72**, 113 (1951).

* The term "amine oxalate (malonate, succinate, and so on) film" is used hereafter as the abbreviation for the monolayer of amine spread on the surface of solution of oxalic (malonic, succinic, and so on) acid.

(22) E. G. Cockbain and J. H. Schulman, *Trans. Faraday Soc.*, **35**, 716 (1939).

(23) Wo. Pauli and L. Sternbach, *Kolloid-Z.*, **84**, 291 (1938).

aqueous tannin[22],[24], silicate[6] and metaphosphate[25] and for amide film on aqueous tannin.[17]

Now we should draw attention to the fact that the interaction between monolayers of stearic acid and the polyvalent salt in the aqueous substrate closely resembles the interaction between amine monolayer and alginate in aqueous substrate, in that both can form a macromolecular complex as has been reported in the case of aluminum stearate.[26]

In this connection, the experimental data upon wettability shown in Table 2 appear to be of much value. Langmuir[27] has found the remarkable wettability of the built-up film of stearic acid and stearate when it was conditioned with the solution of various metallic ions, and explained this phenomenon by the overturning effect of molecules in the film. In the previous report[2] authors have correlated the two-dimensional network in the film with the difficulty of overturning or re-overturning which seems to be one of the chief factors for the wettability of this film. Inaba[5] also arrived at the same conclusion. The high wettability of the built-up film of amine towards a solution of sodium alginate is similar to the case of stearic acid or stearate towards metallic ion solution. The molecules of amine overturn themselves, and are fixed to the alginate ions and form a network of polyoctadecylamine alginate so that the re-overturning is not allowed and an extremely wettable surface results. In the case of amine phosphate, as shown in Table 2, a remarkable rigidity as described already also acts to hinder the overturning of amine molecules and the surface remains non-wettable. Further, we can also see in this table, though not so distinctly, that the resistance to wetting increases with increasing distance between the hydrocarbon chains attached to organic diacids. Again the authors have inclined to the opinion that the easiness of overturning when treated with alginate solution is chiefly determined by the magnitude or complexity of amine~organic acid compound formed in the film.

(24) F. Sebba and E. K. Rideal, *Trans. Faraday Soc.*, **37**, 273 (1941).
(25) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 2400 (1937).
(26) V. R. Gray and A. E. Alexander, *J. Phys. Colloid Chem.*, **53**, 23 (1949); C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949); etc.
(27) I. Langmuir, *Science*, **87**, 493 (1938).

Summary

Attempts were made to transfer the monolayers of octadecylamine on distilled water both onto the metal surface and onto the optical gauge of barium stearate. They did not adhere to the former surface, while with the latter it was shown that the homogeneous film was obtained when the substrate *p*H and the piston pressure were favorable for preventing the film from aggregating.

Effects of organic anions upon the mono- and multilayers of amine were investigated. The increase of the distance between the ionic groups of dicarboxylic acids caused the corresponding expansion and change in thickness of amine monolayer spread on the solution containing these anions. The solution of sodium alginate caused a somewhat large expansion and gave a remarkable rigidity towards the amine monolayer spread on it.

The built-up film of amine transferred from the substrate of various organic acids showed a variety of resistance for wettability when treated with aqueous sodium alginate solution. It was found that the resistance for wetting increased with the increasing complexity of the two-dimensional network formed in the film prior to the treatment. These results were discussed with regard to the easiness of overturning.

The authors wish to thank Mr. T. Tsutsumi for the micro nitrogen analysis of octadecylamine. They also wish to express their thanks to the Ministry of Education for the grant given for this research.

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The Effect of Chain Length, Salts and Alcohols on the Critical Micelle Concentration

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Introduction

The effect of chain length and salts on the critical micelle concentration of colloidal electrolytes was measured by several authors,[1]~[6] and discussed by Corrin[7] and Hobbs.[8] The effect of alcohols and of alcohols and salts on the critical micelle concentration was measured by Corrin, Harkins and Herzfeld.[9][10] However, the theoretical treatment was not completely done. In the present paper, the model of large flat micelle is adopted and the following experimental facts are explained theoretically:

1) The effect of chain length on the critical micelle concentration of paraffin chain salts follows the equation.[1]~[6]

$$\log_{10} C = -K_0 m + K_1 \qquad (1.1)$$

2) The decrease of critical micelle concentration by the addition of salts follows the equation.[6]

$$\log_{10} C = -K_2 \log_{10}(C+C_s) + K_3 \qquad (1.2)$$

3) The effect of alcohol chain length on the critical micelle concentration follows the equation.[9]

$$\log_{10}(\mathrm{d}C/\mathrm{d}C_a) = K_4 m' + K_5 \qquad (1.3)$$

4) The critical micelle concentration is a linear function of the alcohol concentration.[9]

$$C' = -(\mathrm{d}C/\mathrm{d}C_a)C_a + C \qquad (1.4)$$

where C: critical micelle concentration mole per liter

C_s: concentration of added salts in equivalents of effective ion per liter.

C_a: concentration of added alcohols mole per liter.

$K_0, K_1, K_2, K_3, K_4, K_5$: constant and K_0 is nearly equal to 0.3 and K_4 is nearly equal to 0.47 according to the experimental results.

m: number of carbon atoms of the soap molecule.

m': number of carbon atoms of alcohol molecule.

$\mathrm{d}C/\mathrm{d}C_a$: rate of change of critical micelle concentration with alcohol concentration in mole units.

Basic Assumption of the Theory

1) Due to the fact that a nonpolar oil such as benzene or hexane is solubilized between the monolayers of the soap micelle increasing X-ray spacing but showing only a slight effect on the critical concentration,[11][12] we have ignored interaction of the two end discs.

2) In the light of the basic assumption of the Debye theory of the micelle, we may express the total energy change in the micelle formation in terms of the electrical energy and the cohesive energy, and the change of cohesive energy per one molecule by the formation of a micelle is assumed to be proportional to the number of carbon atoms. We express this in term of $m\omega$.

3) With respect to the value of ω, Debye[13] has adopted the heat of vaporization of the hydrocarbon, and he assumed $\omega \approx 2.0\,kT$. But Hobbs,[8] referring to the heat of vaporization, adopted $\omega = 1.0\,kT$ to explain the empirical results. Cassie and Palmer[14] assumed $\omega \approx 0.85\,kT$ or $1.2\,kT$ on the basis of adsorption data of Powney and Addison[15] at the water-xylene interface. We have calculated an approximate

(1) G. S. Hartley, *Kolloid-Z.*, **88**, 22 (1939).
(2) K. Hess, W. Philippoff and H. Kiessig, *Kolloid-Z.*, **88**, 40 (1939).
(3) A. B. Scott and H. V. Tartar, *J. Am. Chem. Soc.*, **65**, 692 (1943).
(4) J. Stauff, *Z. Physik. Chem.*, **183 A**, 55 (1938).
(5) W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).
(6) M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947).
(7) M. L. Corrin, *J. Colloid Sci.*, **3**, 333 (1948).
(8) M. E. Hobbs, *J. Phys. and Colloid Chem.* **55**, 675 (1951).
(9) S. H. Herzfeld, M. L. Corrin and W. D. Harkins *J. Phys. & Coll. Chem.* **54**, 271 (1950).
(10) M. L. Corrin and W. D. Harkins, *J. Chem. Phys.* **14**, 640 (1946).
(11) E. C. Lingafelter, O. L. Wheeler and H. V. Tartar, *J. Am. Chem. Soc.*, **68**, 1940 (1946).
(12) R. W. Mattoon, R. S. Stearns and W. D. Harkins, *J. Chem. Phys.* **16**, 644 (1948).
(13) P. Debye, *J. Colloid Sci.*, **4**, 407 (1949).
(14) A. B. D. Cassie and R. C. Palmer, *Trans. Farad. Soc.*, **37**, 156 (1941).
(15) J. Powney and C. C. Addison, *Trans. Farad. Soc.* **33**, 1243 (1937).

value of ω from the fact that the solubility in water of aliphatic homologous compounds diminishes about 1/3 with the increase of one carbon atom. That is, the following equation is obtained for the homologous aliphatic compounds, since the solubility is thought to be proportional to the exponential of energy change per one molecule when it dissolves:

$$C_n/C_{n-1}\exp(-\omega/kT)=1/3 \qquad (2.1)$$

Where C_n/C_{n-1} is solubility ratio of the homologous aliphatic compounds of n carbon compound to $n-1$ carbon compound.

Calculating (2.1), we obtain

$$\omega=1.08\,kT \qquad (2.2)$$

This value will be referred to later.

The Electrical Potential at the Charged Surface of Lamellar Micelle

If long chain electrolytes are aggregated to the micelle, they will give effectively a plane charge at the micelle surface. The ordinary Debye-Hückel approximation $e\phi/kT\ll1$ can not be used, because the contribution of electrical energy is too large to assume the above condition.[8][14][16] However, for a uniformly charged plane surface the Poisson-Boltzmann equation can be integrated without making this approximation.

$$\frac{d^2\phi}{dx^2}=-\frac{4\pi}{D}\sum z_i n_i e^{-z_i\xi\phi/kT}$$

Where ϕ: electrical potential
x: the direction normal to the surface
D: the dielectric constant of the solution
Z: the valency of ion
n: number of ions per c.c. in the bulk of the solution

Giving the boundary condition and neglecting the contribution of the same ion in the bulk, Hobbs[8] obtained the equation for a uni-univalent electrolyte:

$$\phi=\frac{kT}{e}\log\left\{\frac{1000\,\pi\sigma^2}{2DRT}-\log C_i\right\} \qquad (3.1)$$

Where C_i: total concentration of gegen ion in mole per liter
σ: charge density at the micelle surface
e: electric elementary quantum

The integral work of introducing another charge of e into the surface of the micelle is given by ϕe. However, the alternative is to assume that each molecule contributes less than this because of the adsorbed gegen ions and the electrical potential due to the ion atmosphere in the solution. Accordingly, a factor K_e should be introduced in this equation.

Then, $$(\phi-\phi')e=K_e kT\left\{\log\frac{1000\,\pi\sigma^2}{2DRT}-\log C_i\right\} \qquad (3.2)$$

Where ϕ': the electrical potential in the solution

Statistical Treatment of Critical Micelle Concentration

According to the analogy of the equilibrium condition between vapor and liquid we assumed the equilibrium condition between solute and pure liquid might be given, equating the partial potential of solute and that of liquid (micelle). The partial potential of a soap ion in the micelle is assumed to be.[17]

$$\mu^L=-\chi-kT\log(2\pi mkT)^{3/2}v/h^3-kT \\ -kT\log j(T)+pv^L \qquad (4.1)$$

and the partial potential of a soap ion in the solution may be given by the equation

$$\mu^S=-\chi'+kT\log CNkT/1000 \\ -kT\log(2\pi m)^{3/2}(kT)^{5/2}/h^3-kT\log j'(T) \qquad (4.2)$$

Where v: free volume per one molecule
$j(T)$: partition function for the internal degrees of freedom, to be equal in the two phases
$-\chi$: uniform potential of liquid which is a smoothed value for all relative configurations of the given molecule (ion) and its neighbours, in this time χ contains electrical energy.
C: molar concentration of soap in molecular dispersion

As they are in equilibrium, equations (4.1) and (4.2) are equated, and the following equation is obtained:

$$\log C=\log 1000/Nv-(\chi-\chi')/kT-1 \\ +pv^L/kT \qquad (4.3)$$

(16) D. Edelson and R. M. Fuoss, *J. Am. Chem. Soc.*, **70**, 2832 (1948).

(17) R. H. Fowler and Guggenheim, E. A. "Statistical, Thermodynamics", Cambridge. 1939, p. 329.

Where

$\chi-\chi'$: energy difference between micellar state and solute state, and equal to the summation of cohesive energy change $m\omega$ and the electrical energy change $e(\phi-\phi')$ per one molecule.

At ordinary pressure (concentration), pv^L is negligibly small compared with kT, and might be omitted without loss of accuracy.

Then (4.3) can be written

$$\log C=\log 1000/N\upsilon-m\omega/kT+e(\phi-\phi')/kT-1 \qquad (4.4).$$

This gives critical micelle concentration in unit of mole per liter.

The effect of Salts and chain Length on the Critical Micelle Concentration

Substituting (3.2) into (4.4), we obtain

$$\log C=\log\frac{1000}{N\upsilon}+K_6\left\{\log\frac{1000\,\pi\sigma^2}{2DRT}-\log C_t\right\}-\frac{m\omega}{kT}-1 \qquad (5.1)$$

Introducing the values $\sigma=e/20.5$ A.^{2}, $D=80.8$, $T=291$°K., and $\omega=1.08\,kT$ and assuming $N\upsilon=10$ cc., equation (5.1) becomes

$$\log_{10} C=-K_6\log_{10}(C+C_S)-0.47\,m+1.565+1.686\,K_6 \qquad (5.2).$$

Where C_S: the concentration of added salts and $C+C_S$ is equal to C_t

Comparing this to the experimental equation of Corrin and Harkins[18] for Potassium Laurate:

$$\log_{10} C=-0.5696\log_{10}(C+C_S)-2.6172 \qquad (5.3).$$

We obtain

$$K_6=0.57 \qquad (5.4).$$

It is thus shown that the effect of added salts on the critical micelle concentration is given by the equation (1.2). When no salts was added we obtain from (5.2) and (5.4):

$$\log_{10} C=-0.57\log_{10} C-0.47\,m+1.565+0.96 \qquad (5.5).$$

Then $$\log_{10}C=-0.3\,m+1.61 \qquad (5.6).$$

Where m is the number of carbon atoms constituting a hydrocarbon chain, and for fatty acid soap one carbon atom which organizes carboxyl radical must be excluded. Thus the effect of chain length on the critical micelle concentration, equation (1.1), is explained. However, we must consider work of hydration to represents the experimental results for different head group.

The Effect of Alcohols on the Critical Micelle Concentration

The effect of alcohols upon the critical micelle concentration is a matter of some dispute. Herzfeld, Corrin, and Harkins measured the critical concentration of dodecylammonium chrolide in the presence of ethanol, 1-propanol, 1-buthanol, 1-hexanol, 1-heptanol, 1-decanol, 1-undecanol, 2-propanol, and trimethyl-carbinol.[9] We have measured the critical micelle concentration of potassium laurate in the presence of ethanol, 1-buthanol, isoamylalcohol, 1-hexanol, 1-octanol, 1-decanol, and 2-ethylhexanol by the dye titration method. Many other authors have measured the effect of alcohols on the critical micelle concentration.[19][20]

However, the mechanism by which long chain alcohols depress the critical concentration was unknown. It has been definitely established that the long chain alcohols penetrate into the oriented structure of the micelle.[21] An attempt is made in this paper to explain the effect of alcohols based on the concept of a decreased charge density at the micelle surface neglecting the interaction of the two end discs.

We denote the concentration of soap ion in the solution equilibrium with the soap micelle at the given temperature and pressure by $C_S°$, and the concentration of alcohol molecule in the solution equilibrium with the imaginary alcohol micelle at the given temperature and pressure by $C_A°$, and the concentrations of soap ion and alcohol in the solution equilibrium with the mixed micelle by C_S and C_A respectively. Assuming that the alcohol molecule and the soap ion in the micelle dissolve each other in the state of regular solution. We obtain:

$$C_S\fallingdotseq C_S°N_S/(N_S+N_A)\ldots.N_S/(N_S+N_A)\approx 1 \qquad (6.1).$$

(18) M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947).

(19) G. L. Brown, P. F. Grieger and C. A. Kraus, *J. Am. Chem. Soc.*, **71**, 95 (1949).

(20) A. W. Ralston and D. N. Eggenberger, *J. Am. Chem. Soc.*, **70**, 783 (1948).

(21) W. D. Harkins, R. W. Mattoon and R. Mittelmann, *J. Chem. Phys.*, **15**, 763 (1947).

$$C_A \fallingdotseq KC_A^{\circ} N_A/(N_S+N_A)\ldots N_A/(N_S+N_A) \ll 1 \quad (6.2).$$

Where $N_S/(N_S+N_A)$, $N_A/(N_S+N_A)$ is the molar fraction of soap and alcohol in the micelle. The molar fraction of soap is nearly equal to 1, and K is the constant. As there exists the equilibrium between the alcohol molecule in the water and that in the micelle, the concentration of alcohol equilibrium with mixed micelle is expressed as follows, using (6.2) and according to the analogy of equation (4.3):

$$C_A \propto N_A/(N_S+N_A)\exp\{-(\chi-\chi')/kT\} \quad (6.3).$$

Where $\chi-\chi'=m'\omega$: cohesive energy change per one alcohol molecule.

If we denote molar fraction of alcohol in the micelle by x, we obtain

$$x \propto C_A \exp\{m'\omega/kT\} \quad (6.4).$$

Thus the molar fraction of alcohol in the micelle increases proportionally as the bulk concentration increases. And the concentration of alcohol in the bulk equilibrium with the micelle of given molar concentration decreases about $1/3=\exp(-\omega/kT)$ with the increase of one hydrocarbon chain in the alcohol molecule. As the effect of solubilization on the alcohol concentration in the bulk must be negligibly small at the critical point, the concentration of added alcohol is equal to the concentration of alcohol in the bulk.

On the other hand the equilibrium concentration of soap ion in the bulk decreases, depending on the molar fraction of the soap ion in the micelle and on the decrease of the charge density. When the molar fraction of alcohol becomes x, the molar fraction of soap in the micelle becomes $1-x$, and the charge density decreases from σ to $(1-x)\sigma$.

Thus the critical concentration at the presence of alcohol is expressed using (6.1) and substituting $(1-x)\sigma$ into (5.1). Then we obtain:

$$(1+K_6)\log C' = (1+K_6)\log C + \log(1-x) + K_6 \log(1-x)^2 \quad (6.5).$$

Where C': critical micelle concentration of soap-alcohol mixed micelle, when the molar fraction of alcohol is x.

C: critical micelle concentration of soap micelle in the absence of alcohol

From (6.5) we deduce:

$$C'/C = (1-x)^{1+2K_6/1+K_6} \quad (6.6).$$

When $K_6=0.57$, and the molar fraction x is small compared with unity, we obtain:

$$C'/C \fallingdotseq 1-1.36x \quad (6.7).$$

Then using the equation (6.4), we obtain:

$$(C-C')/C \propto x \propto C_A \exp\{m'\omega/kT\} \quad (6.8).$$

Thus for a given alcohol we obtain the relation:

$$C' = K_7 C_A + C \quad (6.9).$$

Where K_7: always negative

This equation expresses the fact that the critical concentration is a linear function of alcohol concentration, and corresponds to (1.4).

For various alcohol we obtain:

$$\log_{10}(C-C')/C_A = 0.47\,m' + K_5 \quad (6.10).$$

This equation expresses the effect of alcohol chain length on the critical concentration, and corresponds to (1.3). And the decreasing effect by the addition of alcohol is similar with any soap.

Comparison of the Effect of Alcohols with the Experimental Results

According to the data given by Herzfeld, Corrin, and Harkins[9] for dodecylammoniumchloride at 25°C. and those given by the author for potassium laurate at 10°C the rate of change of critical concentration with alcohol concentration is constant for a given alcohol but varies with the kind of alcohol employed.

Table 1 shows the comparison with the experimental data and the calculated values, assuming the rate of change of critical concentration by hexanol is 0.213 molar concentration per mole of alcohol.

Table 1

The Rate of Change of Critical Micelle Concentration in Molar Concentration per Mole of Alcohol

Alcohol	Dodecylammoniumchloride at 25°C.	Potassium-Laurate at 10°C.	Calculated C. M. C.
Ethanol	0.00145	0.00252	0.0026
Fropanol	0.00624	—	0.0079
1-Buthanol	0.0192	0.0258	0.0237
Isoamylalcohol	—	0.070	0.071
1-Hexanol	0.213	0.23	(0.213)
1-Heptanol	0.623	—	0.639
1-Octanol	—	1.87	1.92
1-Decanol	20.2	(8.64)	17.28
1-Undecanol	44.5	—	51.8

Thus the change of the effect of alcohols on the critical concentration has explained based on the solubility ratio of alcohols.

The author thanks to Prof. H. Akamatsu for his suggestion of this problem and Dr. M. Nakagaki for the discussion of the results.

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The Absorption Spectra of Styryl Dyes

By Kazuo SHIBATA

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Spectroscopic properties of polymethine dyes have been the subject of repeated investigations, especially because of the interest concerning the functional relationships between the wavelength of absorption maxima and the length of conjugated systems. It has been known that the cyanine dyes show the absorption maxima that are in approximately linear relationship to the length of conjugated systems, while in the case of polyene dyes, such as diphenyl polyenes, the squares, of the wavelengths of absorption maxima are related almost linearly to the length of conjugated systems. To account for these phenomena several theories have already been proposed, among which the one set forth by Herzfeld and Sklar[1] seems to be most coherent and cogent.

Recently we have reported that the styryl dyes, a category of polymethine dyes which is structurally different from cyanine and polyene dyes, show an intermediate spectroscopic property between those of the latter two groups.[2] It appears, therefore, worthwhile to investigate whether the theory of Herzfeld and Sklar might be extended also to the cases of this intermediate type of polyene dyes.

Experimental

The styryl dyes investigated are listed in Table 1. They were synthesized by the reaction of dimethylamino-benzaldehyde with mono- or di-methylpyridine-iodoethylates or mono- or di-methylquinoline-iodoethylates, using pyperidine as the condensation reagent.*

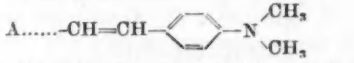
Observations of absorption spectra in a visible region were carried out by the photoelectric method, using an Adam Hilger monochrometer, the accuracy of which was about ±10 A. Throughout the experiments ethanol was used as the solvent.

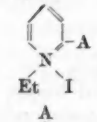
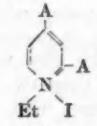
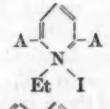
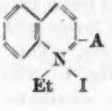
Results and Discussions

The observed values of absorption maxima of the dyes are listed in the third column of Table 1. On examining the data obtained, it becomes apparent that the disubstituted compounds (II), (III) and (VI) have two absorption bands, while monosubstituted compounds (I), (IV) and(V) have only one absorption band in the visible region.

Table 1

The Absorption Maxima of Styryl Dyes

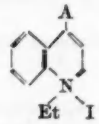


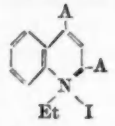
No.	Compounds	$\lambda_{obs.}$(in A.)	$\lambda_{cal.}$(in A.)
I		4670	4880
II		4350 5100	— —
III		4100 4970	4160 —
IV		5270	—

(1) Herzfeld and Sklar, *J. Chem. Phys.* **10**, 508, 521 (1942).

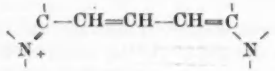
(2) K. Snibata, This Bulletin, **25**, 378 (1952).

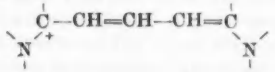
* In the synthesis of disubstituted styryl dyes such as compound (II) in Table 1, certain amounts of monosubstituted compounds were also formed as byproducts. These byproducts were removed by the chromatographic adsorption method.

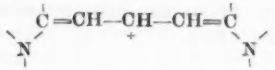
V  5460 5660

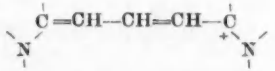
VI  5000 4620 5710 5570

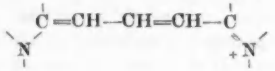
This result is of special interest from the viewpoint of the theory of Herzfeld and Sklar. According to them, the color of symmetric cyanine dyes arises from the transition between the two states caused by the resonance of two ground structures with equal energies. Let us consider trimethine dye (A) as an example of symmetric cyanine dyes. Though quite a number of resonance structures can be assumed by this substance, we may, for the present purposes, restrict our considerations to the following five structures of low energy levels.

 (A)

 (B)

 (C)

 (D)

 (E)

Of these resonance structures, two structures (A) and (E) have equal and lowest energies; that is, the ground level corresponding to the zero-order eigen functions is degenerate. In the first approximation by the method of valence bond eigen function, these two structures may be shown not to interact with each other directly. Their interaction results from the indirect interaction through other structures (B), (C) and (D) with higher energies; namely, (A) interacts with (B), (B) with (C),...., and (D) with (E). As a result of these interactions, the two degenerate ground levels split into two states with different energies. The situation is graphically shown in Fig. 1. The color of symmetric cyanine dyes is attributed to the transition between these split levels.

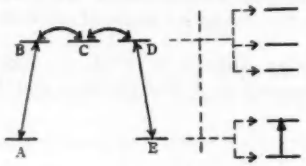
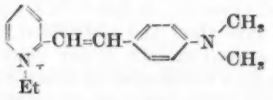
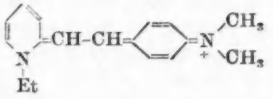


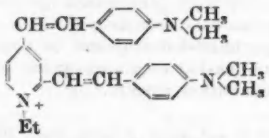
Fig. 1.

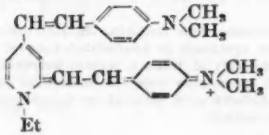
The same line of reasoning may be applied to the interpretation of the number of absorption bands of styryl dyes. For monosubstituted styryl dyes, we may consider two structures with lowest energies apart from the other levels. In contrast to the case of symmetric cyanine dyes, these two structures have slightly different energies, because the molecules are asymmetric. For example, the two resonance structures to be assumed for compound (I) will be

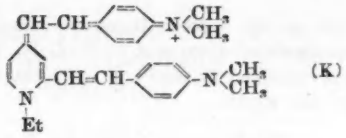
 (F)

 (G)

As a result of resonance, the height of energy levels will be changed, but the resulting levels of these two structures may be considered to be by far lower than those of other higher levels, since we may assume that the levels corresponding to the structure with the formal charge at the carbon atom is sufficiently higher than the levels of the structure with the charge at the nitrogen atom. The same consideration will lead to the inference that the number of levels with rather low energies must be three in disubstituted styryl dyes; for example, the structures to be assumed for compound (II) are as follows:

 (H)

 (J)



(K)

The absorption of light caused by the transitions between (F) and (G) as well as between (H), (J) and (K) may all be in the visible region. Thus, the fact that the monosubstituted dyes show one absorption band and the disubstituted dyes two in tne visible region has received a rational explanation.

On inspecting the data given in Table 1, the following facts will also be noticed.

i) The wavelengths of absorption maxima of the dyes having quinoline nucleus are always greater than those of the corresponding dyes with pyridine nucleus.

ii) The bathochromic effect of the redical A at position 4 of pyridine or quinoline nucleus is always stronger than the effect of the same radical at position 2.

In the preceding paper these relations have been explained on the basis of the "color factor", which was proposed as a convenient parameter to account for the spectral denpendency on the lengths of conjugated systems of many cyanine and polyene dyes. In the following an attempt will be made to elucidate quantitatively the spectroscopic properties of these substances from the viewpoint of the method of valence bond eigen function. It should be noted in advance that we are obliged to make a rather crude approximation because of the complex nature of the molecules of styryl dyes.

Let us consider compound (I) and assume that the energies of the eigen functions corresponding to the structures (F) and (G) are e and f, respectively. We shall neglect the interactions between many states other than (F) and (G) and assume the effective interaction energy between (F) and (G) to be α, though more precisely, these stepwise interactions must be taken into account. The height E of the levels resulting from the resonance in question can be obtained by solving the following secular determinant;

$$\begin{vmatrix} e-E & \alpha \\ \alpha & f-E \end{vmatrix} = 0 \qquad (1).$$

The same assumption will lead to the following equation* (2) for the energy of compound (III).

$$\begin{vmatrix} f-E & \alpha & 0 \\ \alpha & e-E & \alpha \\ 0 & \alpha & f-E \end{vmatrix} = 0 \qquad (2).$$

For compound (II), the interaction energy between (H) and (J) will also be α, but the interaction energy between (H) and (K), which may be denoted by β, must be assumed to be smaller than α, if we take into account the length of the conjugated double bond. Hence, the equation for the energy of the states of compound (II) will be

$$\begin{vmatrix} f-E & \alpha & 0 \\ \alpha & e-E & \beta \\ 0 & \beta & f-E \end{vmatrix} = 0 \qquad (3).$$

The solutions of equations (1), (2) and (3) are graphically shown in Fig. 2, in which dotted arrows indicate resonance.

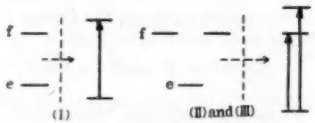


Fig. 2.

Using equations (2) and (3), the values of parameters, α, β and f-e, were calculated from the data of the two absorption bands of compound (II) and the band at the longer wavelength of compound (III). The obtained values ($\alpha = 6258\ cm^{-1}$., $\beta = 5207\ cm^{-1}$. and f-$e = 16228\ cm^{-1}$.) were used for the calculation of the wavelength of the absorption maximum of compound (I) and that of compound (III) at a shorter wavelength.

As to compounds (IV), (V) and (VI), we assumed that the interaction energies α and β are the same as in the above cases but the energy difference f-e has a different value, which was calculated from the data of compound(IV). This value of f-e (f-$e = 14261\ cm.^{-1}$) was assumed to be applicable also to compounds (V) and (VI).

The calculated value of the wavelength of absorption maximum of each compound is shown in the fourth column of Table 1. As will be seen, the coincidence between calculated and observed values is fairly good in spite of the crude approximation we have made. These results seem to substantiate the theory of Herzfeld and Sklar, showing that it may well be applied also to the cases of asymmetric conjugated systems. The results obtained give us also ground for the conclusion that the absorption bands shown by styryl dyes in a

* In this equation, the interaction between the two states, which have the positive charge at the nitrogen atom of amino group, was ignored.

visible region are due to the transition between electronic levels, and not to the transition to the split levels of one electronic level caused by the vibrational splitting.

The author wishes to express his earnest thanks to Dr. M. Katayanagi for his generous gift of the intermediate compounds for the synthesis of dyes, and to Prof. H. Tamiya for his valuable guidance and his constant interest in this study.

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LETTER

A New Microdetermination of Iodide by its Catalytic Reaction

By Iwaji IWASAKI, Satori UTSUMI and Takejiro OZAWA

(Received August 26, 1952)

The authors found that the orange color of ferric thiocyanate which was formed by dilute potassium thiocyanate and an excess of ferric salt in dilute nitric acid solution, faded very slowly owing to the oxidation of thiocyanate, but rapidly in the presence of minute amounts of iodide.

The catalytic action of iodide on this reaction was studied colorimetrically, and a new microdetermination of iodide was accomplished.

Iodine also catalyzed the fading of ferric thiocyanate in exactly the same way as iodide, but chloride and bromide did not. In preliminary experiments it was found that this catalytic reaction was greatly affected by the presence of small amounts of nitrite. The reaction rate depended not only on the concentrations of iodide present, but also on the concentrations of thiocyanate and nitric acid, and especially on the temperature (Fig. 1).

Therefore these factors must be kept constant for iodide determination.

The determination of iodide could be made by measuring the absorbancy in a definite period of time and using the calibration curves (Fig. 1) previously obtained under the same conditions.

Procedure and Results:

To 10 cc. of the sample solution, 1.0 cc. of mixed reagent (3×10^{-3} or 10^{-3} M in potassium thiocyanate, 3×10^{-4} M in sodium nitrite) and 2.0 cc. of ferric alum reagent (prepared by dissolving 6 g. of ferric alum in 100 cc. of 5.7N nitric acid) were added. The absorbancies were plotted against

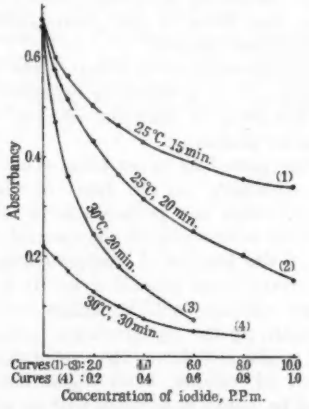

Fig. 1.—Calibration curves of iodide.
Curves (1)-(3): 3×10^{-3} M SCN$^-$
Curve (4): 10^{-3} M SCN$^-$

the concentrations of iodide as shown in Fig. 1.

The absorbancy was determined by a Beckman Model DU spectrophotometer at 460 mμ[1] using 10 mm. cell. The calibration curves shown in Fig. 1 were reproducible within ± 5%.

The determination of iodide in concentrations of 0.5 — 10 p.p.m. could be made under the following conditions: 3×10^{-3} M SCN$^-$, 25°C., 20 minutes (Curve 2). The determination of iodide in concentrations of 0.05—0.8 p. p. m. could be made under the following conditions: 10^{-3} M SCN$^-$, 30°C., 30 minutes (Curve 4).

It was also possible to determine 0.001—0.05 p. p. m. of iodide under the following conditions: 10^{-3} M SCN$^-$, 45°C, 30 minutes.

By this method 0.001—10 p. p. m. of iodide could be determined in the presence of chloride and bromide.

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(1) I. Iwasaki, S. Utsumi and T. Ozawa, This Bulletin. **25**, 226 (1952).

Dielectric Behaviour of Gypsum Crystals and Possibility of their Zeolitic Dehydration

By Ryôiti KIRIYAMA and Hideko IBAMOTO

(Received August. 28, 1952)

We have measured the anisotropy of the temperature and frequency dependences of the dielectric properties of gypsum single crystals. The crystals used were from Hanaoka, Akita Prefecture, Japan.(1)

The dielectric constants at room temperature are as follows: $\varepsilon_{\perp}=5.1$, $\varepsilon_{//}=10$, where $\varepsilon_{\perp}$ is the one perpendicular, and $\varepsilon_{//}$ the one parallel to the cleavage plane.

Temperature coefficients of the dielectric constants from 20° to about 90° C. show slightly positive signs in both directions. Above 90° up to 116°, they show slightly negative signs. Above 116°, the dielectric constant parallel to the cleavage plane at 5 kc rises slowly, and at 124° there is a maximum and then falls gradually, whereas there is no peak at 3 Mc. On the contrary, the dielectric constants perpendicular to the cleavage plane show no peaks at either frequencies. Above about 125°, the dielectric constants in both directions and both frequencies decrease gradually and tend to asymptotic values.

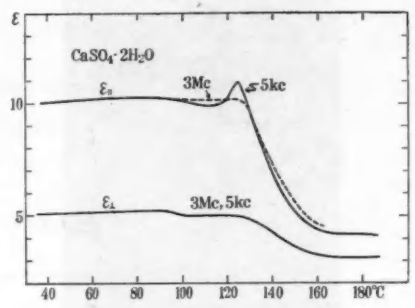
The dielectric loss has been measurable in only one case where a peak of dielectric constant appeared at about 124°.

In many hydrated crystals which we have studied up to this time, their dielectric constants and losses suddenly increase when their lattices collapse and dehydration occurs. These phenomena are due to the protonic conduction in adsorbed water layers of dehydrated crystals.(2)

In the case of gypsum, in spite of its dehydration, there was no remarkable rise of dielectric constants or losses except a low maximum at a low frequency mentioned above.

Then, it may be assumed that in gypsum, when this dihydrate changes to the hemihydrate by partial dehydration, the dehydrated water molecules form no adsorbed layers which are able to transfer protons on the surface.

The newly formed hemihydrate thus will contain water molecules in their crystal lattices as in typical zeolites, and the water molecules evaporate slowly with rising temperature.



Dielectric behaviours of gypsum crystals and possibility of their zeolitic dehydration

The low maximum of the dielectric constant parallel to the cleavage plane at 5 kc may be attributed to the temporary formation of dipole clusters caused by free water molecules in the loosened layer lattice. A phenomenon analogous to it has already been observed by the authors in the case of the dehydration of $K_2HgCl_4 \cdot H_2O$ single crystals.(3)

Department of Chemistry, Faculty of Science, Osaka University, Osaka

(1) The authors wish to thank Dr. Z. Harada and Mr. K. Sakurai for getting large single crystals.

(2) Details will be published elsewhere.

(3) Presented shortly to the 2nd Congress of International Union of Crystallography, 1951. Details will be published.

Photoelasticity of Fe_3O_4 Film isolated from Iron Single Crystal

By Shigeto YAMAGUCHI

(Received september 3, 1952)

The test piece of iron single crystal was etched with an ethanol-bromine (10: 1 by volume) solution. The Fe_3O_4 film (thickness: about 200 A.) formed on the etched surface was isolated from the underlying substrate.(1) The isolated oxide film was placed upon a glass plate and was examined by means of polarizing microscopy. When the specimen was placed between a polarizer and an analyzer set for extinction, some light passed through it and interference effect was observed, which is shown in Fig. 1. Fig. 1 indicates that an isotropic substance Fe_3O_4 (cubic structure, spinel type) is doubly refracting, i.e., under unsymmetrical strain.

(1) S. Yamaguchi, *J. Appl. Phys.*, **22**, 680 (1951); S. Yamaguchi, T. Nakayama and T. Katsurai, *J. Electrochem. Soc.*, **98**, 21 (1949).

Fig. 1.—The micrograph obtained from the Fe_3O_4 film placed between a polarlizer and an analyzer set for extinction. The oxide film contains the doubly refracting domains, since the film retains unsymmetrical strain forced on it while performing a lattice fit with the underlying substrate.

Fig. 2.—Electron micrograph of the oxide film prepared in the same way as for Fig. 1.

Fig. 3.—Electron diffraction pattern obtained from the Fe_3O_4 film of Fig. 2. This pattern shows that the oxide crystallites are oriented relative to the substrate facets.

The oxide film prepared in the same way as for Fig. 1 was magnified by means of electron microscopy (vid. Fig. 2). In Fig. 2 are found the crystal forms reprinted from the etched surface by oxide replica.(2) The figures characteristic of Fig. 2 are similar to those of Fig. 1.

The oxide film of Fig. 2 gave an electron diffraction pattern of Fig. 3, which verifies the presence of regularly oriented crystallites of Fe_3O_4. This regular orientation of Fe_3O_4 crystallites suggests the lattice fit between the Fe_3O_4 crystal and the substrate crystal of iron.(3) The $Fe^{\cdots}$-$Fe^{\cdots}$ distance found in the normal Fe_3O_4 crystal is 8.37 A. (lattice constant of Fe_3O_4), and the doubled value of the distance (4.045 A.) between the nearest two atoms in the (111) planes of iron is $4.045 \times 2 = 8.09$ A. The difference between these two distances is so small (3.5 %), i. e., the strain in the oxide film caused by the underlying substrate is so slight, that the orientation and strain within the oxide film are retained even after the film is divorced from its substrate. As a matter of fact, this isolated film exhibits an anisotropic property, as is shown in the micrograph of Fig. 1, although it is difficult to determine exactly the lattice deformation of Fe_3O_4 film by measuring the diffraction pattern.(3)

The oxide film formed on a mechanically polished surface of iron and isolated from it showed no anisotropic property, distinguishable from that formed on the etched surface of single iron crystal. This oxide film gave a diffraction pattern showing the random orientation of Fe_3O_4 crystallites.

It was here demonstrated, that when a thin film of oxide of cubic structure isolated from a metal surface is doubly refracting, it is composed of oxide crystallites oriented regularly relative to the substrate facets. This photoelastic orientation is given to the oxide film by a slight shift in the lattice fit between the oxide crystal and its substrate.

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(2) S. Yamaguchi, *J. Appl. Phys.*, **22**, 1295 (1951); **23**, 445 (1952); This Bulletin, **24**, 237 (1951); *Nature*, **169**, 19 (1952); cf. *J. Appl. Phys.*, **23**, 935 (1952).

(3) cf. E. K. Halteman, *J. Appl. Phys.*, **23**, 150 (1952).